Pectin: The Miracle Molecule

by

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Abstract

People may know that pectin is the ingredient that thickens jams and jellies, but many people are not aware of its other uses, or even how it works. This paper discusses the structure of pectin, pectin's gelling mechanisms, sources of pectin and manufacturing techniques. Difficulties in manufacturing, and research centered around solving these problems, particularly in the area of de-esterification and structure detection are also discussed. Uses of pectin will be described, including food-related uses, other than jam and jelly production, and its use as a lead-removal aid. A particular focus on health-related benefits of consuming pectin is also included.

Introduction

While many people may know that pectin is the substance that causes jams and jellies to thicken, and gummy candies to be gummy, many do not know that pectin has a myriad of other uses, ranging from other food applications, to industrial, medicinal and pharmaceutical. The versatility of its structure and its omnipresence in land-based plant life make it an inexpensive and effective tool in a wide variety of uses. However, despite the fact that it is found in all land-based plants and is used in such a wide variety of situations, scientists are still discovering new things about this miracle molecule that was first isolated in 1825 by Henri Braconnot (Willats, Knox, & Mikkelsen, 2006). What is it? How is it made? How does it work? Why is it a *miracle molecule*?

Basic Structure of Pectin

Pectin is not one specific molecule, but a class of polysaccharide carbohydrates that encompasses many different structures with a common saccharide as its subunit. There are three major types of chains in pectin (Willats, Knox, & Mikkelsen, 2006), but all three types of pectin chain consist primarily of rings of methylated D-galacturonic acid (Ovodov, 2009). D-galacturonic acid is the oxidized form of D-galactose, in which the sixth carbon, in the R-group external to the saccharide ring, is converted from an alcohol to a carboxylic acid group through oxidation (Mohnen, 2008).

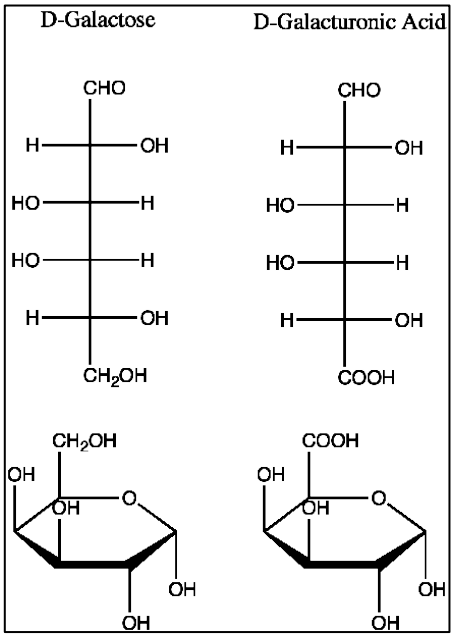


Fig. 1 – Fischer and Haworth projections of D-Galactose and D-Galacturonic Acid

Fig. 1 shows the Fischer and Haworth projections of D-galactose and D-galacturonic acid. The difference is important, because while both D-galactose and D-galacturonic acid are present in plant cell walls, it is the acidic nature of the D-galacturonic acid that provides the charge needed for the strong intermolecular bonding that gives the plant cells, and thus the plants, structure and rigidity (Voragen, Coenen,

Verhoef, & Schols, 2009; Phillips & Williams, 2000).

The D-galacturonic acid (GalA) monomers are connected with a β1,4 glycosidic linkage. In this type of glycosidic linkage, a bond is created through dehydration, using an -OH group from each monosaccharide. The result is an oxygen linking the two monosaccharide units. In pectin, the connection occurs between an equatorial -OH on the first carbon in the ring of one GalA and an equatorial -OH on the fourth carbon in the ring of a second GalA, giving it the designation β1,4. Since the two OH groups involved are equatorial, the linkage creates a linear polysaccharide (Fernandez, 2001).

The three types of chains are classified according to their degree and type of substitution. The first type, called Homogalacturonan (HG), is a simple chain consisting of polygalacturonic acid, with no substitution. Due to its lack of substitution, HG pectin chains are often referred to as "smooth" chains. The second type of chain, called Rhamnogalacturonan I (RG-I), has a backbone of alternating GalA units and α-D-Rhamnose (Willats, Knox, & Mikkelsen, 2006) (see **Fig. 2**). Unlike HG pectin, which has β1,4 glycosidic linkages along the entire chain, RG-I backbones are linked with β1,2 (C1 on the GalA, C2 on the Rha) and β1,4 (C1 on the Rha and C4 on the GalA) linkages (Willats, Knox, & Mikkelsen, 2006) (see **Fig 3**). This method of linking introduces kinking into the chain, which can result in a helical shape, determined by the type and degree of substitution (Sriamornsak, 2003). Substituents in RG-I tend to be varying lengths of glycan chains, most commonly consisting of Arabinose or Galactose (Willats, Knox, & Mikkelsen, 2006). The third major type of pectin chain is called Rhamnogalacturonan II (RG-II). RG-II has an HG backbone that is

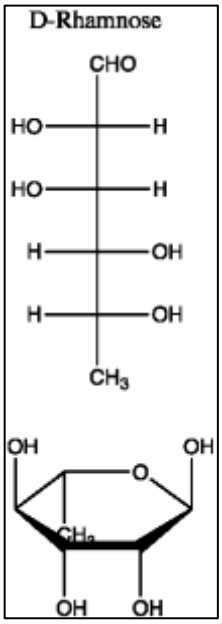


Fig. 2 – Fischer and Haworth projections of D-Rhamnose

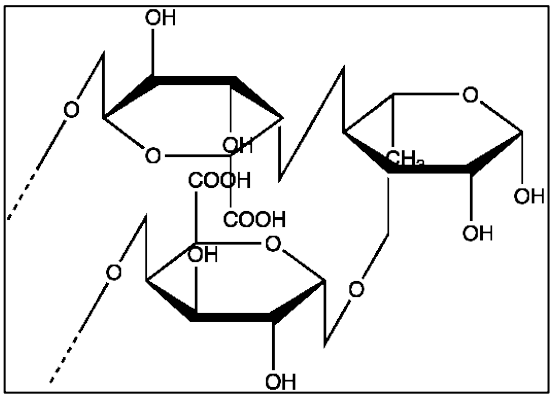


Fig. 3 – A unit of Rhamnogalacturonan I (RG-I) showing the alternating β1,2 and β1,4 glycosidic linkages that introduce kinking into the chain's structure.

substituted with a wide variety of complex glycan side chains, containing a variety of neutral sugars. RG-I and RG-II, due to their high degree of substitution, are often referred to as "hairy" chains (Willats, Knox, & Mikkelsen, 2006).

Originally, it was thought that HG chains make up the primary backbones of pectin molecules, with RG-I and RG-II pieces inserted into the HG chains. However, scientists are now suggesting that RG-I may be the primary backbone, and HG and RG-II are major side chains of the RG-I backbone (Willats, Knox, & Mikkelsen, 2006). **Fig 4** is a schematic that shows this model.

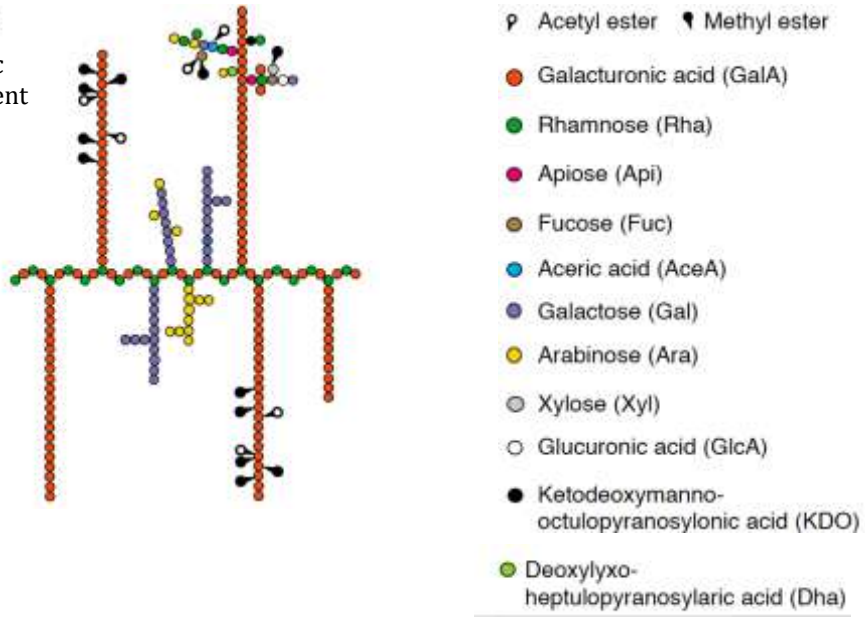


Fig. 4 – Schematic showing the current model for pectin molecule chains (Willats, Knox, & Mikkelsen, 2006).

In addition to the side chains on RG-I and RG-II, pectin molecules also have a certain amount of methyl-esterification and acetylation on the GalA units (May, 2000). Methylation of the galacturonic acid monomers in pectin occurs when the carboxylic acid group is esterified with a methyl group, and helps to determine the functionality of the pectin molecule, since it has an effect on the type and magnitude of intermolecular bonding that occurs (Fernandez, 2001). A carboxylic acid functional group consists of a carbon that is double-bonded to an oxygen, single-bonded to an -OH group, and single-bonded to the associated R-group. An ester is a carbon that is double-bonded to an oxygen, and single-bonded to each of two R-groups. In the methyl esterification of pectin, a methyl group (CH_3) replaces the hydrogen on the OH group on the carboxylic acid, changing the R group from COOH to $COOCH_3$ (**Fig 5**). Acetylation occurs when the carboxylic acid is converted to a particular type of ether called an acetate (**Fig 5**).

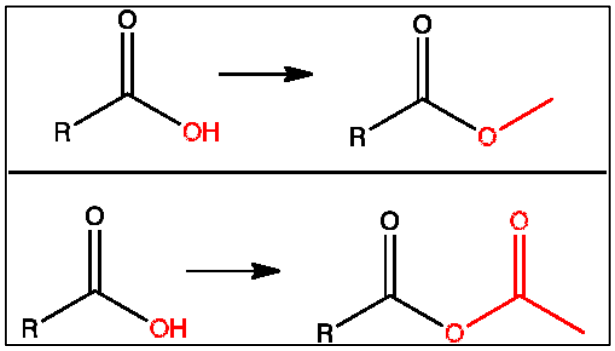


Fig. 5 – Change in molecules due to methyl-esterification (top), and acetylation (bottom). Changes highlighted in red.

During the esterification process, the carboxylic acid group of each GalA unit may, or may not be esterified, and the pectin chain is classified according to its level of methyl-esterification. If the ratio of esterified to non-esterified units (called the degree of esterification, or DE) is greater than 1:1, then it is called high ester, or HM (for high-methoxyl) pectin. If the ratio of esterified to non-esterified units is less than 1:1, then it is called low ester, or LM (for low-methoxyl) pectin. Since the DE is important to the function of the pectin molecule, the DE is always specified when discussed (Sriamornsak, 2003). Commercially, LM pectin is most commonly manufactured by putting HM pectin through a de-esterification reaction in an acidic environment (CP Kelco, 2001). In addition to HM and LM pectin, there is also a type of commercially-produced (it does not occur naturally in plants, as HM and LM pectin do) pectin called Amidated pectin (ALM pectin), in which some of the non-esterified carboxylic acids are converted into acid amide groups (CP Kelco, 2001). The processes for manufacturing LM, HM and ALM will be discussed in more detail later.

Pectin Gelation

Pectin's utility in food, industry and pharmaceuticals (medical applications are centered around the shape and nature of the molecule, itself) is primarily centered around its ability to form gelatins, which translates into its ability to hold onto water, its ability to thicken, and its ability to stabilize (CP Kelco, 2001). Pectin gels are hydrocolloids, mixtures involving water, in which one substance is suspended in another. The concept of gelation can be simplified by thinking of it as a substance that involves partial precipitation and partial dissolution (May C. D., 1990). Carbohydrate-derived hydrocolloids tend to rely upon intermolecular bonds being created to connect long sugar chains, to other sugar chains, or to other parts of the same sugar chain (**see Fig. 6**). This interaction causes the creation of pockets that can trap water and solutes, thus creating the colloid (**see Fig. 7**) (Phillips & Williams, 2000).

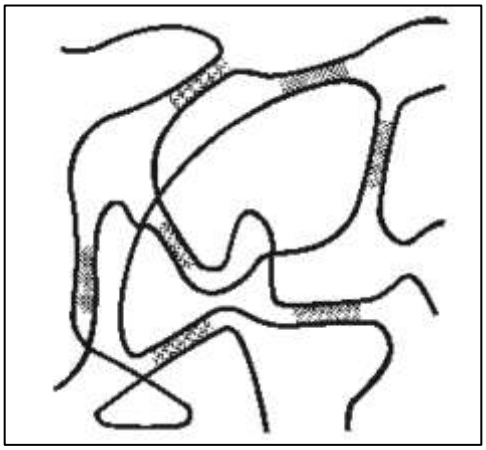


Fig. 6 – A schematic of the intermolecular bonding in pectin molecules. The shaded parts represent regions of bonding (CP Kelco, 2001).

This interaction can be manipulated by changing the pectin molecule, itself, the pH and conentration of the solution (of pectin and/or cosolute, usually sugar), and temperature of the gelling environment. **Table 1** shows the different intermolecular interactions that occur in the gel, and which help to determine the gel's properties, and its formation. Gels with specific properties can be created by manipulating these interactions.

	Polymer	Water	Cosolute (sugar)

Polymer	Polymer-Polymer	Polymer-Water	Polymer-Cosolute
Water	Water-Polymer	Water-Water	Water-Cosolute
Cosolute	Cosolute-Polymer	Cosolute-Water	Cosolute-Cosolute

Table 1 – The intermolecular interactions that occur i pectin gelation process. The highlighted interactions most important, and that can give gels particular attri through manipulation.

In the case of pectin, the two most important interactions to look at are the polymer-polymer interactions, and the polymer-water interactions. The polymer-polymer interactions are important, because those are what create the bonds between pectin chains. The polymer-water interactions are important, because pectin's level of hydrophobicity is determined by the DE (Agoub, Giannouli, & Morris, 2009), as the ester substitutent is fairly hydrophobic, whereas the polar carboxylic acid substituent is hydrophilic. The cosolute-water interactions come into play as competition for the polymer-water interactions. The more cosolute there is in the solution, the less the water is available to dissolve the pectin. The cosolute-cosolute interactions affect gelation, because some sugars bond directly to the pectin, which impedes bonding between pectin chains by taking up bonding sites. Other cosolutes congregate around the pectin molecules, creating areas that are conducive for pectin-pectin bonding (Agoub, Giannouli, & Morris, 2009).

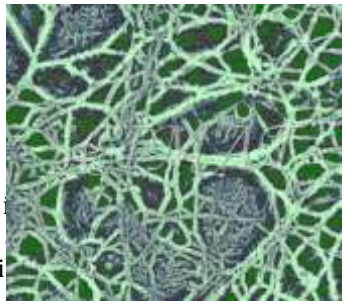


Fig. 7 – Microscope image of pectin complex showing the pockets created by bonding of sugar strands. The pockets trap water and solutes, creating the colloid (Electron Microscopy of Food and Microorganisms, 2008) .

In addition to DE, molecular weight plays a role in gelling. When polymerized, pectin can have a wide range in numbers of galacturonic acid units, ranging from a few hundred units to around one thousand units. This wide range in chain length is reflected in a large range in molecular weights (Sriamornsak, 2003). The longer the chain is, and the higher the molecular weight that results, the greater the strength of the intermolecular bonding that occurs. This increase in the IMF results in a more viscous product, thus stronger gels (Fernandez, 2001). It is, however, important to note that high DE, which would result in a decrease of molecular weight, also results in strong gels. Therefore, the effect of molecular weight is largely due to the increase in sheer magnitude of London Dispersion Forces between the chains.

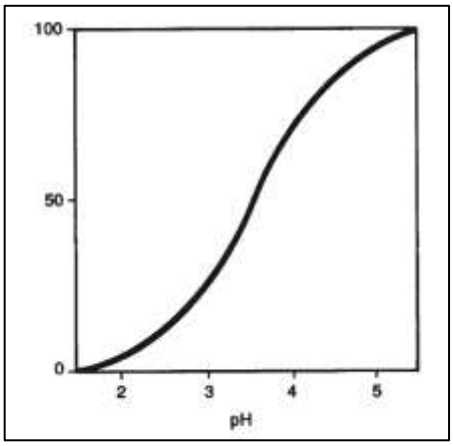


Fig. 8 – Pectin dissociation curve showing estimated pKa of 3.5 (CP Kelco, 2001).

Of the three types of pectin (HM, LM, Amidated), HM is the least versatile, because it has the most specific requirements for effective gelation. HM pectin needs specific combinations of pH level and sugar concentration. The higher the pH, the more sugar needs to be in the solution for gelation to occur. At higher pH, the unesterified GalA units, which still have carboxylic acid groups exist as deprotonated COO^-, as a result, they usually found as ion salts at higher pH. While exact pKa values for pectin dissociation are difficult to establish, it is generally believed to be in the range between pH 3.5 to pH 4.5 (**see Fig. 8**)(Rolin, Nielsen, & Glahn, 1998) As pH is decreased, the COO^- converts to COOH, thus reducing electrostatic repulsion. This has the result of allowing the pectin chains to come closer together, thus allowing hydrogen-bonding to occur (Agoub, Giannouli, & Morris, 2009). As the electrostatic repulsion decreases, the level of sugar in the solution can be decreased as well, since less water needs to be bound up to keep from interacting with the pectin molecules (May C. D., 1990).

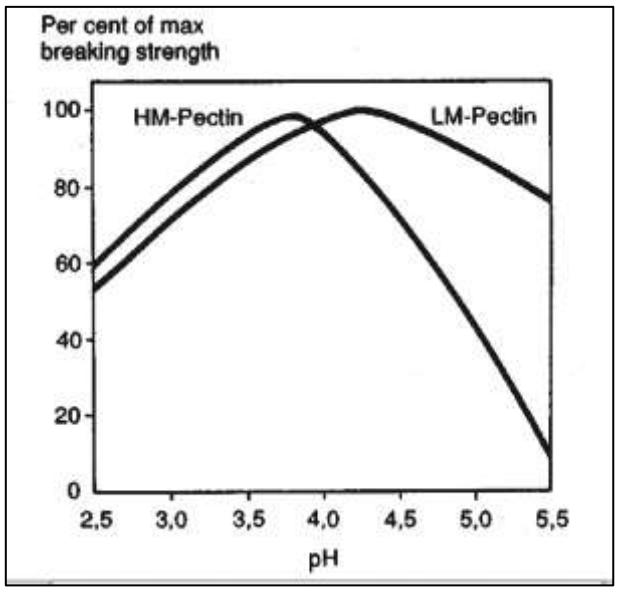
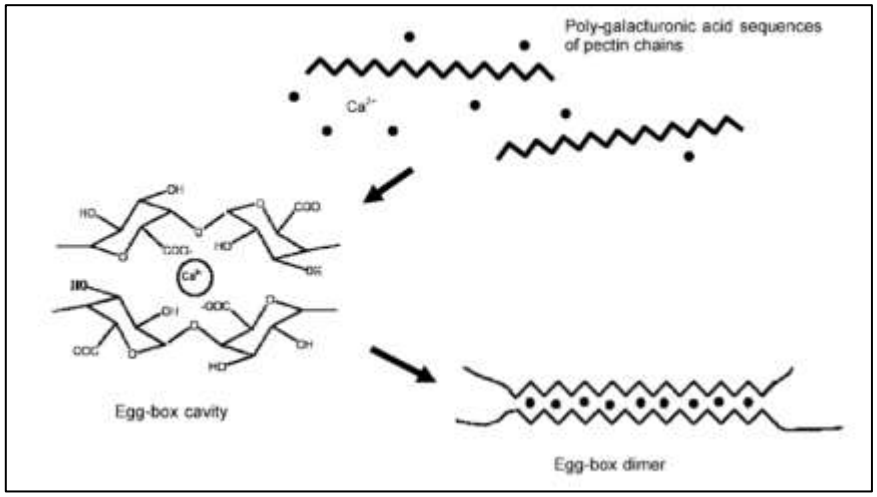


Fig. 9 – Graph showing the change in gel strength when exposed to 90° C temperature for fifteen minutes, at different pHs (CP Kelco, 2001).

In addition to inhibiting gelation, higher pH solutions also create a weaker gel at higher temperatures--one with lower-than-desired viscosity, and tensile strength. **Fig. 9** shows the change in maximum breaking strength when HM-pectin gels and LM-pectin gels are exposed to 90°C temperatures for fifteen minutes, at varying pH. The LM-Pectin gel strength stays above 50% of maximum, while the HM-pectin gel peaks at approximately pH 4, and then drops precipitously, to reach less than 10% of maximum strength at pH 5.5 (CP Kelco, 2001).

The flipside, and the positive aspect of HM pectin's bonding qualities, is one that is used to great effect in products such as candy-making, and anything that requires long-term stability, namely its maintenance of its gel structure once the gelation process is complete, even in high-temperature environments. This is due to its use of hydrogen-bonding, and its hydrophobicity (May C. D., 1990), both of which are temperature independent.

Unlike HM pectin, LM pectin can be dissolved after gelation is complete. This is due to the fact that LM pectin's and Amidated pectin's intermolecular bonding occurs through the creation of dimers (the linking of two of the same type of molecule), using divalent cations, such as Ca^{2+}, rather than through hydrogen-bonding.



Effective gelation increases as the level of de-esterification increases, as long as the concentration of cations increases at a corresponding rate. In addition, gel strength increases as the level of regularity of de-esterified units increases (May C. D., 2000).

The cross-linking occurs when two HG chains line up, and are then cross-linked with a divalent cation between a $-COO^-$ on each of two additional GalA units, one from each chain. This format of cross-linking, called the *egg-box model*, using two carboxylic acid groups, is why gelation increases with increased regularity in de-esterification. The cross-linking cannot occur with esterified GalA units (Tho, Sande, & Kleinebudde, 2005). **Fig. 10** shows the creation of the dimer through cross-linking.

Amidated pectin, also referred to as Amidated LM pectin, due to its low DE, bonds in the same way as LM pectin, using divalent cations to create dimers. ALM pectin, however, is able to form strong gels by lowering pH, as well, even at lower temperatures. LM pectin, on the other hand, will gel, but not strongly (Capel, Nicolai, Durand, Boulenguer, & Langendorff, 2006).

It should be noted that while most scientists agree on the "eggbox" crosslinking model, which was borrowed from the model of the behavior exhibited by alginates, scientists are not in complete agreement over why the crosslinking occurs (Siew & Williams, 2005). While many view it simply as an ionic bond occurring between the anion on the carboxylic acid and the cation, it has been proposed that the bonding may actually be an effect of charge annihilation. This is believed, because experiments that involved measuring charge density showed that charge density was dramatically reduced in gels, suggesting that the gelling was being allowed to happen, through the reduced steric hindrance that occurred as a result of the reduced charge density from the charge annihilation (Siew & Williams, 2005).

Fig. 10 – A diagram showing the dimerization of two HG pectin chains, consistent with the cross-linking found in LM pectin gelation. The upper portion illustrates the unlinked chains of identical nature in solution with the divalent cation, Ca^{2+}. The chains line up, and are linked with the cation, creating the "eggbox" seen at the lower right (Tho, Sande, & Kleinebudde, 2005).

Food Fakeout:
An olive is an olive, is NOT an olive???

Fig. 1 Hervé This, chemist and progenitor of the molecular gastronomy movement.

When is an olive not an olive? Answer: It's not an olive when it's made by Ferran Adrià, Hervé This, or any of the "molecular gastronomists" who are disciples of Chef Adrià and scientist, This. In the case of the olive, when a diner bites into the "olive" he finds that it is not an olive at all, but actually a globule of olive puree encased in a gelatinous film.

Molecular gastronomy, a term coined by This, who is currently (among other titles) the Scientific Director of the Fondation Science & Culture Alimentaire in France's Académie des Sciences, is the study of chemical properties, and how those chemical properties, such as the chemical properties of pectin, can be used to make new and innovative foods. Not to be confused with food chemistry, which is largely the realm of large-scale food manufacturers, molecular gastronomy is focused on the task of understanding chemistry to be able to create better and/or more innovative individual dishes in restaurants, or at home.[1]

This, along with his research partner, Oxford physics professor, Nicholas Kurti, started the movement in 1988, when they sought to raise the art of cooking to a higher level by increasing the understanding of the cooking process at the molecular level. This also sought to dispel myths about cooking and cooking processes, with the hopes that a better knowledge of chemistry and molecules would lead chefs to be able to do things like make unappetizing foods that are nutritious more appetizing. His final stated goal was to make the pursuit of molecular research and science more interesting to those that had not, themselves, chosen a science career.[1]

Ferran Adrià, chef owner of the world-renowned Michelin three-star restaurant, El Bullí, is credited with being among the first chefs to completely embrace the use of molecular gastronomy as an entire concept for a restaurant, and remains one of the most prominent. In fact, Adrià is so devoted to the importance of finding new cooking techniques that he closes El Bulli for several months a year to work in a laboratory, experimenting with different compounds, and to consult scientists, like This. The fake olive is an Adrià creation that is a development on another of his inventions, fruit caviar.[2]

Fig. 2 Ferran Adria, chef owner of El Bulli and one of the leaders of the molecular gastronomy movement.

That olive? The fake olive owes its existence to alginate, a kelp extract that, like pectin, is a polymer made up of a large number of one type of sugar, chained together.[3] Sodium alginate is combined with olive puree, which is then dropped into a solution of calcium chloride.[4] When the globule comes in contact with the calcium chloride, the sodium alginate's negative charge and the positive charge of the calcium in the calcium chloride allow the polymer chains to crosslink, meaning the polymers line up, nest together, and then create intermolecular connections that take advantage of the attraction between the negative charge and the positive charge. This nesting and crosslinking is what causes the material to gel.[5] The longer the reaction is given, the more gelling takes place, as the molecules become more ordered, and thus more like a solid than a liquid.

Try it yourself! Interested in giving molecular gastronomy a try? Here is a recipe and directions for how to make fruit caviar. Once you've mastered the fruit caviar, the fake olive is just a step away, since it uses a similar technique, only adjusted slightly to accommodate for the larger size of the final product.

This recipe is copied from the website, StarChefs.com. It is an adaptation from a demonstration that Chef Adriá did at the 2003 Lo Mejor de la Gastronomía.[6]

Apple Caviar
Chef Ferrán Adriá
Adapted by StarChefs
Yield: 10 Servings

Ingredients:

Apple Juice:	1 ¼ pounds golden apples
Apple Reduction:	¾ pound Granny Smith apples
Caviar:	8 ounces Apple Juice
	½ teaspoon sodium alginate
	1/8 teaspoon citric acid
Calcium Chloride:	2 cups water
	½ teaspoon calcium chloride

Food Fakeout, cont. –

Fig. 3 A selection of fruit caviars.

Apple Caviar Recipe, cont. –

Garnish: 4 Granny Smith apples, peeled, cored and very cold
½ teaspoon cinnamon
3/8 teaspoon balsamic vinegar

Preparation Method:

For Apple Juice:
Wash and core apples and cut into quarters. Purée apples and pour liquid into a tall and narrow container. Freeze about 30 minutes so that the impurities solidify and rise to the top. Remove from freezer and extract impurities with a skimmer. Strain juice and reserve.

For Apple Reduction:
Wash and core apples and cut into quarters. Purée apples and pour liquid into a tall and narrow container. Freeze about 30 minutes to solidify impurities, which will rise to the top. Remove from freezer and extract impurities with a skimmer. Strain juice and place over medium heat until reduced to caramel consistency.

For Apple Caviar:
While cold, mix 1/3 of juice with Sodium Alginate in blender until Sodium Alginate has dissolved. Heat mixture to 205°F, then remove from heat and stir in remaining juice. Add baking soda and stir to dissolve. Strain and freeze until service.

For Calcium Chloride:
Dissolve the calcium chloride in water and reserve.

To Serve:
Purée Granny Smith apples and freeze in a very tall and narrow container 5 minutes. Fill 4 syringes with apple solution. Release one drop at a time into Calcium Chloride and cook 1 minute in water. Strain and rinse caviar in cold water bath. Drain and add 2 teaspoons of Apple Caviar. For each serving, put ¾ ounce of caviar in a cylindrical mold, season caviar with a little Apple Reduction, cinnamon and 3 drops vinegar. Seal and serve.[6]

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Figures

Fig. 1 - Herve This in Macau. http://www.consulfrance-hongkong.org/spip.php?article2969 (accessed July 2009).
Fig. 2 - H. B. A Rat in the Ratatouille. http://www.typicallyspanish.com/news/publish/article_10403.shtml (accessed July 2009).
Fig. 3 - E-Gullet Forums. http://forums.egullet.org/index.php?showtopic=120151 (Accessed July 2009).

Sources and Manufacture of Pectin

All terrestrial plants contain pectin, which binds with cellulose, and creates protopectin, a substance that gives plants their structure. Given this role, it should not be surprising that pectin is found primarily in the plant cell walls, and in the region between cell walls, called the lamella, where it assists in the binding of one cell wall to another. In addition to giving plants their structure, pectin has other important roles, such as determining how porous the cell is, and its pH. Since pectin is so important, it should also not be surprising that pectin is the highest percent composition component, at approximately 35% of a plant's mass (Voragen, Coenen, Verhoef, & Schols, 2009).

Pectin Content of Selected Fruits and Vegetables (adapted) (Fernandez, 2001)

Food	**Pectin content (g/100g)**
Apple	.39 - .49
Apple pomace	15 – 20
Banana	.55 - .68
Beans	.43 - .63
Carrots	.72 – 1.01
Cherries	.40
Grapes	.7
Grapefruits	.65
Kiwifruit	.85
Lemons	.63
Oranges	.57
Sugar beet pulp	15
Sunflower heads	25
Sweet potato	.81

Table 2 – This table (adapted from Fernandez, 2001), shows how much pectin, on average, can be obtained from various sources. Depending on the manufacturing techniques more or less may be extracted (Fernandez, 2001).

As a plant matures, the protopectin, which is insoluble, is broken down by the enzymes pectinase and polygalacturonase and hydrolyzed. This process, started by the enzyme pectin methylesterase, creates a low methyl pectin that is the substrate for polygalacturonase. The physical manifestation of this process can be seen in such things as ripened fruits and vegetables, and released leaves on deciduous plants. In fact, the sweeter taste of the ripened form of many fruits is due to different polysaccharides, such as pectin, getting broken down into their monosaccharide subunits. Since more mature plant materials and fruits have had some time to be exposed to these enzymes, the pectin is not highly desirable for extraction, as their will be fewer long chains, and the level of esterification will be harder to determine (Mohnen, 2008) (Vicens, Fournand, Williams, Sidhoum, Moutounet, & Doco, 2009).

While it is not completely understood how pectin is produced in plant cells, it is believed that the process occurs in the Golgi apparatus (Sterling, Quigley, Orellana, & Mohnen, 2001). It is believed that single GalA units, linked to UDP (Uracil Diphosphate), enters the lumen of the Golgi apparatus, where it goes through a process that removes the UDP, giving an available bonding site for the GalA unit to bond with an existing HG chain. The UDP then loses one of the phosphates, and exits the Golgi apparatus as UMP (Sterling, Quigley, Orellana, & Mohnen, 2001). **Fig. 11** is a schematic of this process.

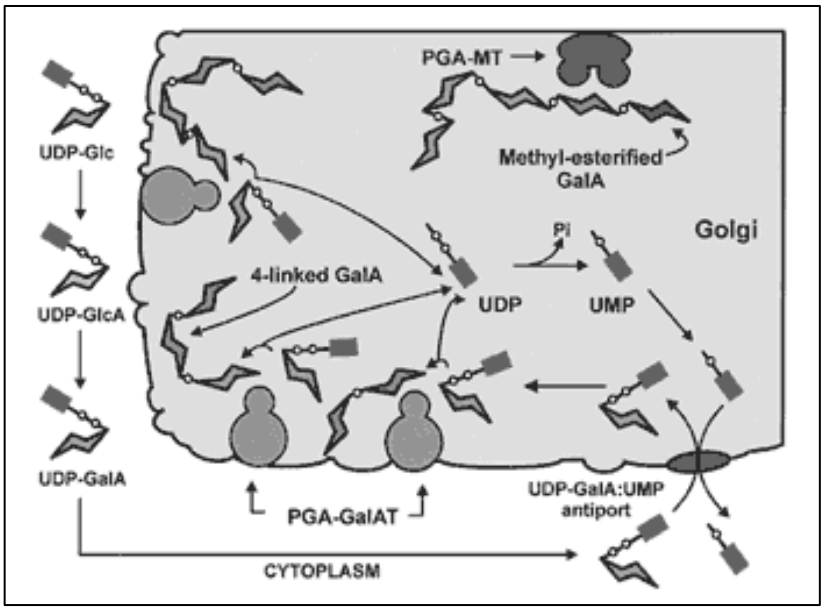

Fig. 11 – A schematic of the process of pectin chain creation in the Golgi apparatus (Georgia, 2006).

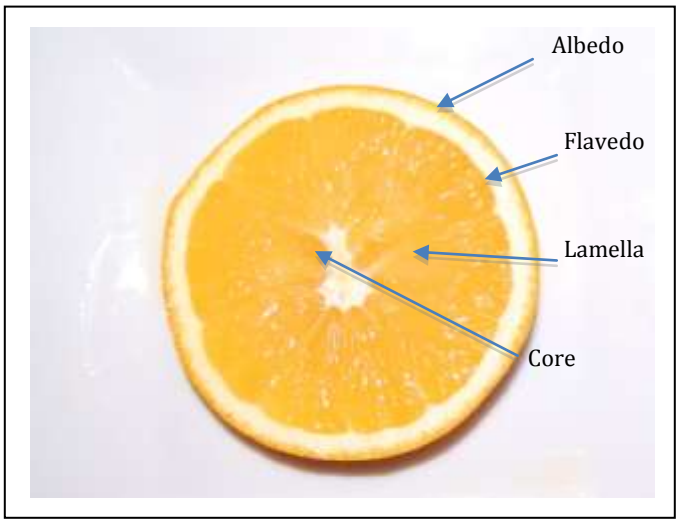

Fig. 12 – A picture of an orange, with labels for the portions where the most pectin is found. The parts of the orange that hold the most juice have the least amount of pectin (CP Kelco, 2001).

How much pectin is present in a plant varies greatly, based on the environmental conditions where the plant is grown, how long it is allowed to mature, and the variety of plant, itself. In commercial pectin production, the primary sources are apple pomace, in which pectin is present in high amounts--up to 20 grams per 100 grams of source material. Apple pomace is the byproduct of apple juice production, and is all the solid material remaining after juice extraction (Fernandez, 2001). Low

quality apples that are not fit for either sale as whole fruit, or for juice can also be used (Rascon-Chu, Martinez-Lopez, Carvajal-Millan, Ponce de Leon-Renova, Marquez-Escalante, & Romo-Chacon, 2009). Citrus peel, also a byproduct of juice production, is the other major source of industrial pectin, exhibiting extraction weights of approximately 20 grams per 100 grams of source material (Fernandez, 2001). Here, the parts that hold the most pectin are not the parts that contain juice, but instead the peel and the core (**see Fig 12**).

Even though there are other plants and fruits that may have a higher percent compositions of pectin, the composition of the pectin, itself may be undesirable, perhaps with excessive amounts of RG-II chains, or not enough long HG chains. **Table 3** shows several products and the percent composition of pectin of each, and how a source that is overall high in pectin levels is not as high in the desirable HG pectin chains as another source that exhibits less overall pectin content. Since conformation is so important to pectin gelation, starting with a source that has a high percent composition of the desired product is more efficient (Willats, Knox, & Mikkelsen, 2006).

Table 1 Occurrence and proportions of the various structural elements in natural products

	Black currant[a]	Bilberry[a]	Grape[b]	Soybean[c]	Sugar beet[c]	Apple[c]
Total polysaccharides (% of dry matter)	19	12	11	16	67	20
Pectic substances (% of total PS)	61	33	56	59	40	42
Structural element (% of pectic substances)						
Homogalacturonan	68	65	65	0	29	36
Xylogalacturonan	0	0	n.a.	21	<1	4
Rhamnogalacturonan I	5	6	10	15	4	1
Neutral side chains	24	27	23	60	48	47
Rhamnogalacturonan II	3	2	2c	4	4	10

n.a. = not analyzed
[a] From Hilz [142]
[b] Recalculated from Nunanet al. [143]
[c] From Voragen et al. [110]

Table 3 – Table of several pectin sources, their respective total pectin composition, and % composition of different pectin chains (Fernandez, 2001).

For instance, sugar beet pectin, acquired as a waste product of sugar manufacturing, does not gel well, even though it has an incredibly high percent composition of pectin, due to the low molecular weight of the pectin, when extracted (May C. D., 2000). However, since it does have a fairly high capacity for holding water, as well as fairly high viscosity, scientists are looking for other applications (Buchholt, Christensen, Fallesen, Ralet, & Thibault, 2004). Another source high in pectin, but problematic in manufacturing, is sunflower heads, a byproduct of the production of sunflower oil. Pectin extracted from sunflower heads has both a high ability to hold water and a high viscosity, and has the

desired high molecular weight, and low degree of esterification. However, sunflower seed heads are traditionally harvested after the heads have fully matured, to make the removal of the seeds easier. At this point, mold has often infected the heads, which will then stimulate the production of pectin methylesterase, an enzyme that breaks down the pectin chains (May C. D., 2000), and which is actually the enzyme responsible for the ripening of fruits and vegetables.

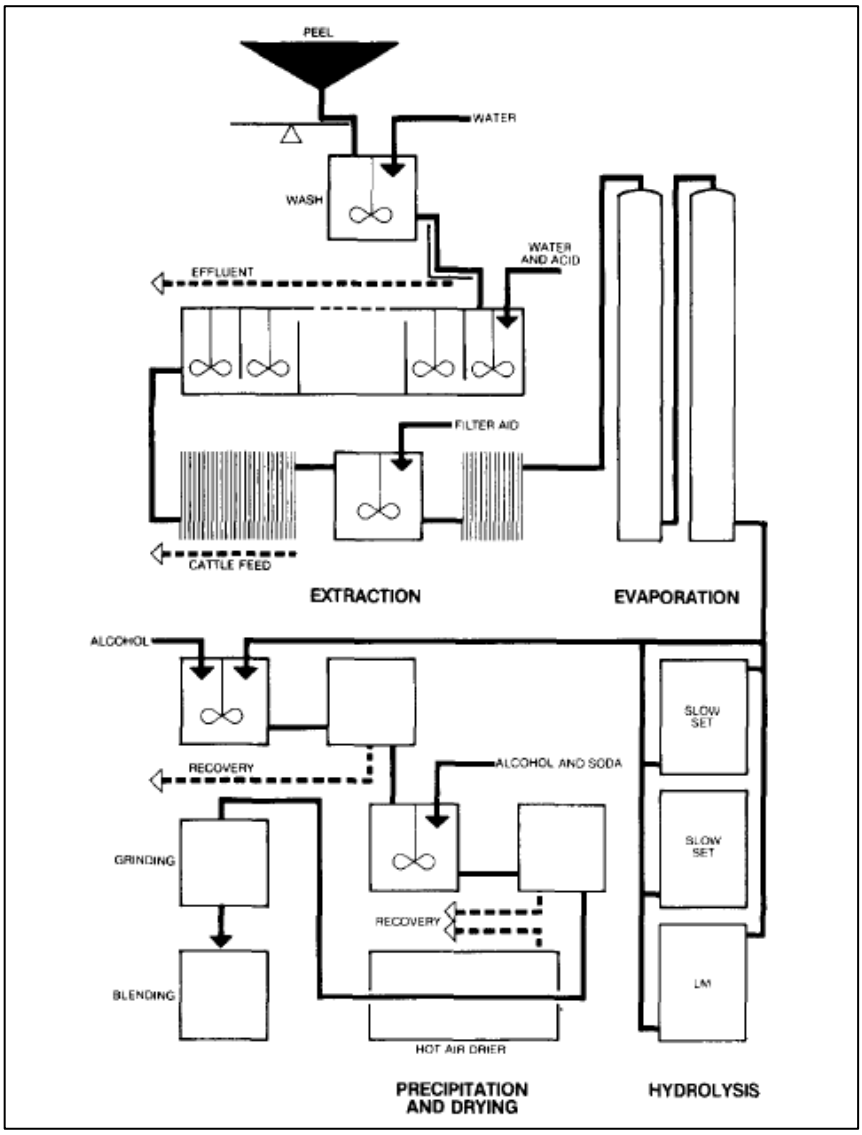

Fig. 13 – A schematic of the manufacturing process (May C. D., 2000).

In fact, it is this problem that makes it particularly important to take into account storage conditions once the source material is acquired. Since citrus peels and apple pomace are both wet materials, fungus and mold can be an issue. This is a particular problem, because both fungus and mold can initiate the production of pectin methylesterase, which will then start degrading the pectin material (May C. D., 2000). In order to keep this process from starting, even in the short time that it might take to ship the wet material from the juice-processing plant to the pectin-processing plant, manufacturers will dry the material directly after juice extraction. In its dried state, it is stable for a much longer period of time, though the heat

applied during the drying process can have the result of a minor degradation of product (May C. D., 2000).

The specifics of the extraction process greatly determine the DE of the pectin that is acquired from the source material. However, the basic steps are the same in all pectin manufacture, regardless of the final product desired. **Fig 13** is a schematic that depicts the process. The four basic steps are as follows (CP Kelco, 2001) (May C. D., 2000):

1. The pectin is extracted from the source material by mixing the source material in hot acidified water, usually around pH 2. The source material determines how long the source material must stay in the acid bath (May C. D., 2000).
2. The liquid pectin that has been extracted is purified via centrifuging and filtration. The number of centrifugation and filtration cycles is determined by how pure (free from original source material solids) it needs to be, which is itself determined by the final use of the pectin (CP Kelco, 2001).
3. If necessary, it is then precipitated from solution with alcohol if the pectin solution is concentrated (from 2-4%) or aluminim salt if the solution is dilute (.3-.5%). When aluminum salt is used, aluminium pectinate is produced, which must, in turn, be washed with acidified alcohol to acidify the aluminum pectinate, which is then neutralized with alcohol with slight basicity (CP Kelco, 2001). However, using alumnium salt has the benefit of causing the pectin to flocculate and rise to the top of the solution, making it easier to skim the product, which is relatively pure at that point (May C. D., 2000). The process of precipitation produces a clump of gelatin strings, which must then be pressed, dried and then ground into powder.
4. At this point of the process, the pectin produced is HM pectin. In general, the highest DE that can be extracted through current large-scale extraction processes is around 75%. If LM pectin or amidated pectin are required then de-esterification of HM pectin to produce LM pectin, or amidation for amidated pectin must occur. It is important to maintain a low temperature if an alkaline bath is used to de-esterify the pectin, because a higher temperature can result in a reaction called β-elimination, in which glycosidic linkages are broken, resulting in much shorter

chains, or worse, single sugar molecules, rather than the desired long HG chains (May C. D., 2000).

Since the method of de-esterification can have a profound effect on the final product, both in terms of the pattern of de-esterification on the chain, itself, and the gel that is produced when the de-esterified pectin is used, scientists are trying to find other methods of de-esterification that do not require such fine-tuned environments. Studies in which de-esterification was conducted via plant pectinmethylesterase (PME) resulted in clumps of de-esterified GalA units alternating with clumps of esterified GalA units. De-esterification via fungal PME resulted in fairly even spacing of esterified and de-esterified units. De-esterification using addition of a base (specifically, NaOH) tends to result in regions with evenly distributed de-esterification, and regions of clumped de-esterification. When submitted to compression tests, the differences in the esterification patterns resulting in different gelation could be seen in the different types of failure. While one type may result in crack forming, another type might result in a decrease in placisticity (Willats, Knox, & Mikkelsen, 2006). **Fig. 14** shows a schematic of the de-esterification by enzymatic methods, and a picture of the difference in gelation resulting from the different de-esterification processes.

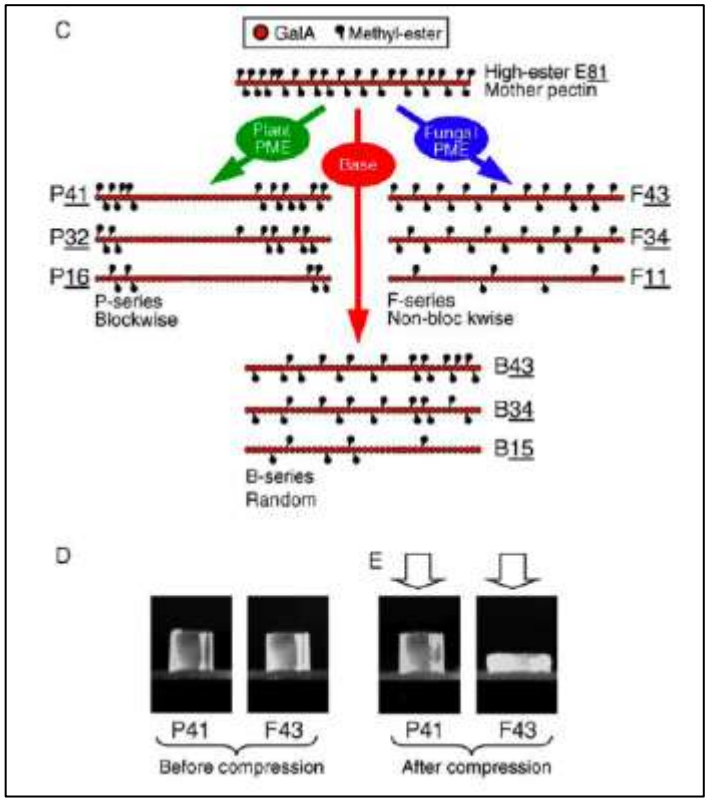

Fig. 14 – Schematics of the patterns of de-esterification caused by different types of enzymatic de-esterification, and pictures of the resulting gels (Willats, Knox, & Mikkelsen, 2006).

Other studies suggest that pectin that has been enzymatically de-esterified have increased industrial utility, because they are more responsive to salt-induced gelation,

which generally produces stronger gels, HM pectin gels that can be melted with heat, and HM pectin gels that will form even at low temperatures, and without added sugar solute (Yoo, Fishman, Savary, & Hotchkiss, 2003) (Yoo, Lee, Savary, Lee, & Hotchkiss, 2009). In addition, enzymatic de-esterification can be conducted at any pH, without β-elimination occurring, making it much less necessary to fine-tune pH during the de-esterification process (Duvetter, et al., 2006). Both the ability to gel at low temperatures, and any pH can be seen as particularly important, given the amount of degradation of gel that can occur with high temperatures and non-acid pH. **Table 4** shows the increase in the reaction rate of β-elimination, and demethoxylation (de-esterification at increasing temperatures. At lower temperatures, demethoxylation happens at a faster rate than β-elimination. At higher temperatures, demothoxylation is still happening at a faster rate than β-elimination, but at a much smaller ratio. Having a de-esterification system that keeps β-elimination from occurring would be highly advantageous (De Roeck, Duvetter, Fraeye, Van Der Plancken, & Sila, 2009).

T (°C)	pH	β-elimination k_β (10^{-6} M/min)	Demethoxylation k_d (10^{-6} M/min)
70	6.37	0.69 ± 0.071	5.63 ± 0.268
80	6.34	1.81 ± 0.066	12.37 ± 0.306
90	6.31	7.83 ± 0.488	30.30 ± 1.570
100	6.28	14.70 ± 0.376	51.71 ± 3.449
110	6.25	29.95 ± 2.652	80.47 ± 6.739
120	6.22	45.03 ± 4.728	133.84 ± 9.642
	E_a (kJ/mol)	96.6 ± 7.8	70.8 ± 3.8

Table 4 - Table showing the increasing reaction rates of β-elimination and demethoxylation with increasing temperatures. While the rate of demethoxylation is always faster than β-elimination, the ratio decreases with increasing temperatures (De Roeck, Duvetter, Fraeye, Van Der Plancken, & Sila, 2009)

In addition to finding new methods for de-esterification, new ways to detect DE are being researched, including use of chromatography, mass spectrometry, Fourier transform infrared spectroscopy, FT-RAMAN, and other spectroscopy tools (Willats, Knox, & Mikkelsen, 2006). One method, in particular that is showing promise is using microarray technology, similar to the technology used in studying proteins and nucleotides (Sorensen, Pedersen, & Willats, 2009). In this method, chains are broken into pieces, and microarrays are made that are then passed through a microarray printer that prints patterns of dots, each of which reflect a particular pattern, for instance HG pectins tend to be printed as rings. The number and arrangement of the dots then indicate the number and placement of

the different types of chains and level and pattern of esterification, in the same way that the microarray printer can analyze and print the pattern of protein or nucleotide chains (Sorensen, Pedersen, & Willats, 2009).

Another detection method that is showing promise uses Atomic Force Microscopy (Ovodov, 2009). In situations in which it is important to see the pectin molecule, as a whole, using AFM is superior to using microarrays, because the use of microarrays, by its nature, requires breaking up the pectin chains for analysis. When using AFM, the molecules can stay intact. Subsequently, it is possible to compare whole molecules. For instance, a fruit or vegetable could be put through two different processing methods, after which the pectin molecules could be examined using AFM, to see what effect, if any, the different manufacturing methods may have on final product (Ovodov, 2009).

Uses of Pectin

Worldwide pectin consumption is increasing at an incredible rapid rate, almost tripling in the past ten years, from approximately 18000 metric tons at the end of the 20th century (Fernandez, 2001), to over 45000 metric tons today (Willats, Knox, & Mikkelsen, 2006). The reason why, is because pectin is an incredibly versatile substance with a wide range of applications, not just in the food manufacturing, but also in industrial processes, and even more importantly, in medicine and pharmaceuticals.

In food, pectin is most often used in jams, jellies and candies. In fact, the bulk of pectin that is used in the world goes towards one of those three applications (Sriamornsak, 2003). However, there are many other food applications. LM pectin is used in yogurt to control texture, fruit distribution and color, and in canned fruit and fruit syrup processing to stabilize long-term texture (CP Kelco, 2001). HM pectin is used in fruit juice concentrate to stabilize or thicken and in bottled fruit juice to increase viscosity or create a more "natural" mouth feel (Wicker, Ackerley, & Hunter, 2003). Sugar beet pectin, which (as stated previously) makes poor gels, works very well as an emulsifying agent for oil/water emulsions (Nakauma, et al., 2008). It does this by coating the lipid molecules, protecting the hydrophobic lipid molecules from the water, and keeping them from wanting to clump to get away from the water molecules (Nakauma, et al., 2008).

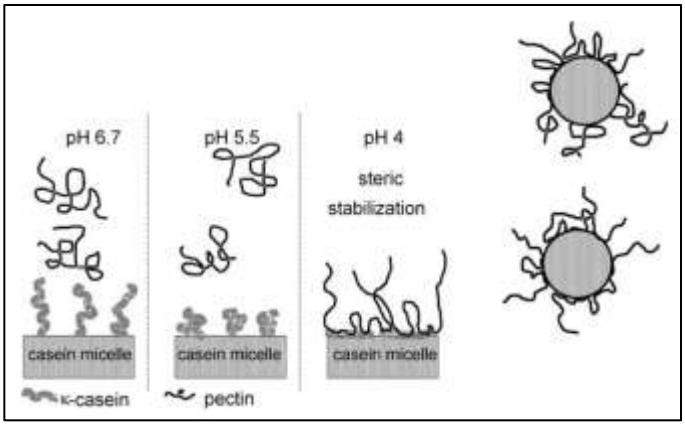

Fig. 15 – A schematic of the coating of casein micelles with pectin to stabilize an acidified dairy drink (Tromp, de Kruif, van Eijk, & Rolin, 2004).

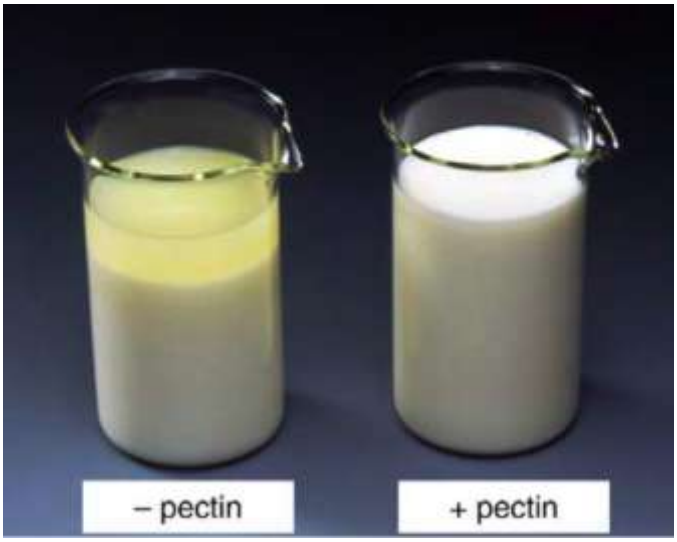

Fig. 16 – A picture of acidified milk drink not stabilized with pectin (left0, and stabilized with pectin (right) (Willats, Knox, & Mikkelsen, 2006)

It is this same process that makes pectin useful in stabilizing acidified milk products, as well (Tromp, de Kruif, van Eijk, & Rolin, 2004) (Laurent & Boulenguer, 2003). As the dairy drink (for instance, buttermilk or Keffir), becomes more acidic, the caseine micelles start to clump together. When the pH reaches approximate pH 5, the calcium that would inhibit clumping is soluble, and the casein micelles clump together, irreversibly (Laurent & Boulenguer, 2003). In order to keep this from occurring, pectin can be mixed into the milk drink. Like in the oil/water emulsion, as the pH lowers, the pectin coats the hydrophobic casein micelles, keeping them from clumping together. The coating, plus the resultant electrostatic repulsion keeps the casein micelles apart, and distributed evenly throughout the liquid (Tromp, de Kruif, van Eijk, & Rolin, 2004). **Fig. 15** shows a schematic of the coating of the casein micelles, and **Fig. 16** shows a picture of the difference between an acidified dairy drink that has not been stabilized with pectin, and one that has.

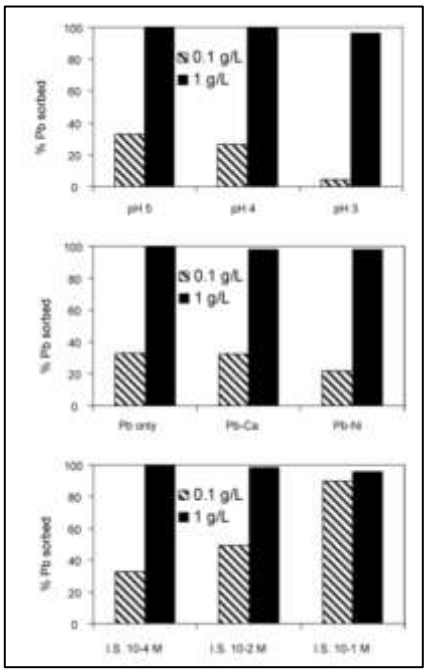

Fig. X – Graphs showing percent biosorption of lead by pectin in citrus peels (Schiewer & Balaria, 2009)

Industrially, pectin has been put forth as a non-toxic tool for flocculation in wastewater and drinking water management. Currently, flocculation is largely conducted by adding some form of hydroxide. The problem with this method is there is a certain amount of toxicity in the process. Using pectin, which is completely biocompatible, would not have the resulting toxicity issues (Schiewer & Balaria, 2009). **Fig. 17** is a series of graphs showing percent biosorption of Pb^{2+} by pectin in citrus peels at varying pH, with different co-ions, and different electrolyte concentration. Furthermore, studies have shown pectin to be highly effective in removing lead from blood, after ingestion (Vasilenko, Klimova, & Lazaryan, 2003). Studies in which lead levels in experimental rats' blood, bone and tissue was measured before and after administration of pectin showed a marked decrease, in some cases to almost none. **Table X** shows the original lead content in the animals, and the lead content after four and eight weeks. While it is not completely understood why it works, scientists hypothesize that it has to do with charge. This is supported by the fact that at decreasing pH, lead removal is less effective. As stated previously, the GalA units deprotonate at approximately 3.5. Higher than this, the carboxylic acid substituent exists

TABLE 2. Effect of Pectin and Laminaride on Lead Content in Biological Substrates of Lead Poisoned Rats

Biomaterial	Lead content in intact animals, %	Lead content (%) in animals treated with lead acetate (1 week) and 0.9% NaCl (control)		Pectin	
		4 weeks	8 weeks	4 weeks	8 weeks
Femoral bone	4.83 ± 0.45	7.05 ± 0.65 $P_1 < 0.02$	6.84 ± 0.53 $P_1 < 0.02$	3.58 ± 0.25 $P_1 < 0.05$ $P_2 < 0.001$	1.57 ± 0.14 $P_1 < 0.001$ $P_2 < 0.001$
Epiphysis	4.95 ± 0.44	7.49 ± 0.62 $P_1 < 0.01$	6.97 ± 0.64 $P_1 < 0.05$	3.83 ± 0.24 $P_1 < 0.05$ $P_2 < 0.001$	1.64 ± 0.18 $P_1 < 0.001$ $P_2 < 0.001$
Breast bone	2.88 ± 0.25	6.84 ± 0.61 $P_1 < 0.001$	6.33 ± 0.55 $P_1 < 0.001$	3.68 ± 0.25 $P_1 < 0.05$ $P_2 < 0.001$	1.43 ± 0.16 $P_1 < 0.001$ $P_2 < 0.001$
Femoral muscle	0.11 ± 0.01	0.15 ± 0.01 $P_1 < 0.02$	0.14 ± 0.008 $P_1 < 0.05$	0.08 ± 0.005 $P_1 < 0.05$ $P_2 < 0.001$	0.07 ± 0.002 $P_1 < 0.01$ $P_2 < 0.001$
Liver	0.03 ± 0.002	0.07 ± 0.005 $P_1 < 0.001$	0.15 ± 0.01 $P_1 < 0.001$	0.17 ± 0.01 $P_1 < 0.001$ $P_2 < 0.001$	0.69 ± 0.05 $P_1 < 0.001$ $P_2 < 0.001$
Kidney	0	0.03 ± 0.001 $P_1 < 0.001$	0.05 ± 0.002 $P_1 < 0.001$	0.15 ± 0.01 $P_1 < 0.001$ $P_2 < 0.001$	0.48 ± 0.04 $P_1 < 0.001$ $P_2 < 0.001$
Urine	0.05 ± 0.003	0.12 ± 0.01 $P_1 < 0.001$	0.21 ± 0.02 $P_1 < 0.001$	0.41 ± 0.04 $P_1 < 0.001$ $P_2 < 0.001$	1.65 ± 0.15 $P_1 < 0.001$ $P_2 < 0.001$
Blood	0.04 ± 0.001	0.06 ± 0.004 $P_1 < 0.001$	0.09 ± 0.006 $P_1 < 0.001$	0.17 ± 0.01 $P_1 < 0.001$ $P_2 < 0.001$	0.56 ± 0.05 $P_1 < 0.001$ $P_2 < 0.001$
Skin with wool	0.05 ± 0.005	0.09 ± 0.008 $P_1 < 0.01$	0.12 ± 0.01 $P_1 < 0.001$	0.13 ± 0.01 $P_1 < 0.001$ $P_2 < 0.02$	0.27 ± 0.02 $P_1 < 0.001$ $P_2 < 0.001$

Table 5 – Table showing the reduction in lead levels due to administration of pectin (right two columns) and lead levels in control group, given NaCl (middle two columns). P_1 and P_2 are probabilities of differences from the data for intact control (Vasilenko, Klimova, & Lazaryan, 2003)

as COO^-. This would readily bond with the Pb^+ ions. Once the pectin bonds to the lead, it then passes through and out of the system, since the only enzymes in the body that can break down pectin are in the colon (Vasilenko, Klimova, & Lazaryan, 2003).

I Scream, You Scream, We All Scream for Hydrocolloids!

Ice Cream! In the 1980's, Breyer's Ice Cream ran an advertising campaign that highlighted the fact that its only ingredients were, "pure milk, fresh cream, [and] sugar." The campaign had different people and children reading the ingredients of "other" ice cream brands, and stumbling over, or being noticeably turned-off by, the ingredient list that included items such as carageenan, sodium alginate, and locust bean gum. The purpose was to imply that the best and most tasty ice creams were those that did not employ food additives (Breyers), and that those ice creams that did resort to using food additives (most other brands) were at best untasty, and at worst full of bad-for-you chemicals, but what are these additives, really? Are they truly *unnatural*? What purpose do they serve in ice cream production, anyways?

Fig. 1 The ingredients list from a Breyer's ice cream carton. Notice that there is now an added ingredient—"natural tara gum" --that serves the same function as any of the other hydrocolloids used in other brands.

What is a *hydrocolloid*? First, it is important to understand that ice cream, itself, is a type of mixture called a *colloid*. A *colloid* is a mixture in which particles of one substance are suspended in another substance, and a *hydrocolloid* is any colloid involving water[1]. Some, like pectin, are made up of polysaccharides, meaning they are made up of chains of a particular sugar. Some are made up of proteins. Ice cream is a complex hydrocolloid in which casein, which is a type of protein, fat globules, air bubbles and ice crystals are suspended in a sugar solution[2]. The ice cream is given volume when the fat globules clump together, but before the clumping can happen, the protein that encases the fat globules, and that stabilizes the fat in the milk, needs to be removed by a compound called an emulsifier[2,3].

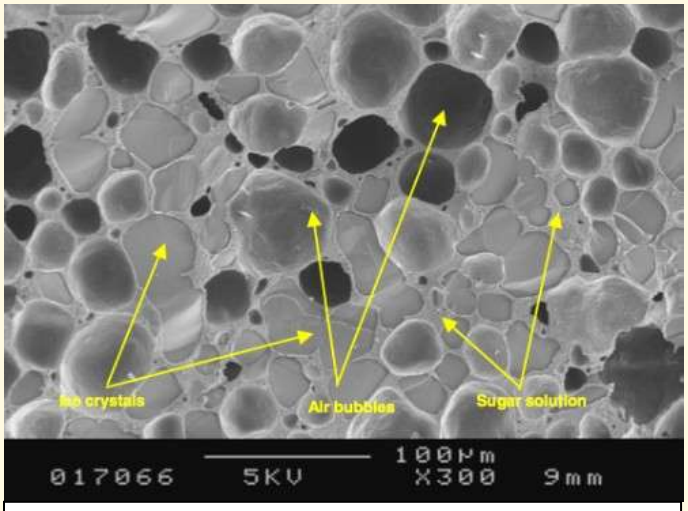

Fig. 2 A scanning electron miscrope image of ice cream. The arrows on the left point to ice crystals, the middle arrows point to air bubbles, and the arrows on the right point to sugar solution.^

Think of what happens when oil and vinegar are mixed to make salad dressing. If they are only lightly mixed, they will quickly separate into globules of oil, floating on the surface of the vinegar. This is what would happen if the fat globules were not surrounded by the casein. However, in order for the fat globules to stick together in the ice cream, the casein needs to be removed. This is where the emulsifier comes in. In some ice creams, egg is used, functioning the way egg works in a Caesar salad dressing. In other ice creams, another fatty molecule is used, such as the one in the ingredient list in the table below[2,3].

So what about those hydrocolloids? The most common hydrocolloid additive in ice cream is carrageenan, which is extracted from different types of seaweed, and is usually present in amounts less than 100-200 ppm (parts per million). Other hydrocolloids that are used are guar gum, agar, locust bean gum, xanthan gum, and sodium alginate, all of which, like carrageenan are present in extremely small amounts. All, except for xanthan gum, are plant extracts[2].

Formulation 5.4 Typical ice cream mix

Ingredients	%
Butterfat	8.00–10.00
Milk solids non-fat	11.10–10.80
Sugar	10.00
Corn syrup solids	3.50
Carrageenan (kappa)	0.015–0.025
Other hydrocolloids (guar gum, locust bean gum, xanthan gum, sodium alginate)	0.10–0.20
Emulsifier (glyceryl monostearate)	0.20–0.50
Vanilla flavour	as required
Water	to 100.00

Table 1 This table shows the ingredients found in most ice creams, and the percent of total solids for each ingredient. The highlighted ingredients are the hydrocolloid food additives, which total less than .25% of the total[1].

Why are these additives used? The primary reason that hydrocolloids are used as additives in ice cream is that they tend to be much more stable molecules than the ice cream molecules, themselves. When these food additives are mixed with the ice cream, they stabilize the mixture, helping the ice cream to remain "creamy" for a longer period of time. It does this in three primary ways. First, the hydrocolloid helps the air bubbles to maintain their shape. The air bubbles help to give the ice cream its fluffy consistency. Without the air bubbles, the ice cream would seem somewhat syrupy. The second way the hydrocolloid assists is that it can hold onto the water molecules more firmly than the ice cream molecules can. Good ice cream has small ice crystals. The larger the ice crystals, the grainier the texture of the ice cream. If the water starts separating from the mixture, it starts forming larger ice crystals in the freezer's temperatures. Finally, the hydrocolloid prevents any further separation of the remaining casein, which, if it occurred, would cause more water to be available to create more of those undesirable large ice crystals[3].

Ice Cream . . . cont -

Do they affect the taste? Some people believe that hydrocolloids adversely affect the taste of the ice cream. However, given the amounts that are used (remember, 100-200 ppm), combined with the fact that most hydrocolloids have a neutral taste, it is highly unlikely that they contribute flavor to the overall product. Furthermore, some hydrocolloids, like carrageenan have the specific purpose of maintaining flavor, by protecting the stability of the air bubbles that, in addition to giving the ice cream structure, help control the release of flavor. So do these hydrocolloids affect taste? Sure, but not in the negative way that people believe[4].

So what's the point? Ultimately, the idea to take from this is a healthy skepticism of any food advertising campaigns. Take the time to learn about the science behind the food, rather than blindly excepting the statements made by the advertisements. Ice cream is just one example of many in the food industry. What does it really mean to be *organic*? What does it mean to be *all-natural*? What does it mean to be *low fat*? What is *lower fat*? Take the time to do the research, and learn what the reality is, and then sit down and enjoy a nice creamy bowl of hydrocolloids. I'll be having a bowl of mint chocolate chip.

Images

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Pectin Use and Health

Pectin shows its true status as miracle molecule when its medical applications are examined. Many might remember the product, Kaopectate, which used to use as its primary ingredient, pectin. Indeed, pectin is particularly useful at stopping diarrhea, particularly in children and babies (Sriamornsak, 2003). Its ability to absorb water and slow the progress of food through the digestive system also makes it a natural, non-toxic diet supplement. In addition, pectin slows food absorption by coating the food molecules, making them less susceptible to digestive enzymes, since only the enzymes in the colon can break down the pectin molecules, and also thickening the coating on the intestinal walls, making it more difficult for the small intestines to absorb the food molecules that have been broken-down (Sriamornsak, 2003). Injecting pectin into wound sites speeds up the process of coagulation (Sriamornsak, 2003), and using pectin as a coating for pills that target the colon allow the medicine to pass through the system until it reaches its targeted area (Liu, Kramer, Fishman, & Hicks, 2003). Recent studies have proposed pectin as a

natural polymer for healing bone fractures, or even making artificial bones (Ichibouji, et al., 2008). Studies have also shown that consumption of pectin reduces DNA damage in laboratory rats (Barth, et al., 2005). Pectin's medical benefits are not just limited to these, and each year we discover more ways that pectin can improve our health.

Gene Therapy Delivery - Amidated pectin is currently being studied as a possible vehicle for use in gene therapy. Currently, the primary delivery system that is used is different modified viruses. The problem with this method is those that arise from the fact that the vehicle is a virus. Even though they are non-pathogenic, they can still have biocompatibility issues, and cause undesirable immuno responses, in which the body would try to rid itself of the entire package, which would result in destruction of the gene therapy, in addition to the viral vehicle. Pectin, however, has high biocompatibility and low immunogenicity, meaning that the body would readily accept the pectin without treating it as a foreign or invasive organism. There have been successful studies in which pectin was seen to join itself readily to DNA strands, suggesting that it would be a highly effective tool for transfer of material from the carrier to the DNA. In order to increase efficiency in bonding, scientists have found that using modified Amidated pectin was necessary, due to the increase in cationic nature. In non-modified Amidated pectin, the amine group is a primary amine. The scientists quarternized the pectin, with the result of having a maximum amount of amidated GalA units. This maximized the cationic nature, which results in an apparent increase in DNA affinity (Katav, Liu, Traitel, Goldbart, Wolfson, & Kost, 2008).

Reducing Inflammatory Response – Nitric oxide synthase (iNOS) and cyclooxygenase 2 (COX-2) are both associated with causing responses in cells that are pathways that lead to multiple medical problems, ranging from inflammation to cancer (Chen, et al., 2006). Various medication have been put forth to try and suppress the response to these enzymes, but many have been shown to be problematic. The use of two in particular, the COX-2 inhibiters Vioxx and Celebrex, showed such an increase in side effects such as stroke and heart attack that their respective companies voluntarily removed them from the market (Drug Safety and Availability: COX-2 Selective (includes Bextra, Celebrex, and Vioxx) and

Non-Selective Non-Steroidal Anti-Inflammatory Drugs (NSAIDs), 2009). Studies have shown that pectin is highly effective in reducing the effect of both iNOS and COX-2 by inhibiting their ability to start the process of produces and replicating harmful proteins. HM pectin, especially those in excess of 90% esterification, were found to be most effective (Chen, et al., 2006).

Table 4 Effects of Pectin Intake in Reducing Plasma and Liver Cholesterol Concentrations in Different Species

Species	% Pectin	% Cholesterol	Weeks	Reduction Total/LDL	Reduction in liver (%)
Rat					
	3	1	4	30/36	36
	7	—	4	27/ND	17
	5	0.25	4	15/ND	None
	8	—	2	16/none	ND
	8	1	2	44/59	ND
	10.5	—	4	13/ND	13
	SBF				
	5	—	3	20/none	ND
	2.5	1	4	22/ND	32
	10	2	1 1/2	32/ND	11
	10	—	1 1/2	12/ND	42
	5	1	4	19/ND	50
Guinea pig					
	2.5 PPP	0.25	4	30/33	48
	1.0 PPP	0.25	4	26/34	57
	12.5	0.04	4	32/ND	19
	12.5	0.25	4	66/70	66
	12	0.17/low fat	4	23/25	16
	12	0.17/high fat	4	30/26	18
female	12.5	0.04	4	30/36	26
female	12.5	0.25	4	30/30	28
Hamster					
	Apples	—	4	None	66
	8	0.4	6	None	None
Swine	12 SBF	—	4	None	ND
Monkey					
rhesus	8 g/day	Fat P/S 2.2	3	18/ND	ND
vervet	14%	Western diet	34	NS	ND

ND, not determined; SBF, sugar beet fiber; PPP, prickly pear pectin; NS, not significant.

Table 2 Effects of Pectin Doses on Plasma Cholesterol Reduction in 12 Human Studies

Subjects	Pectin dose	Type of pectin	Plasma cholesterol reduction (%)	Weeks
10 healthy	15 g/day	LMP	−18	5
10 healthy	15 g/day	HMP	−16	5
9 healthy	40–50 g/day	Pectin	−13	2
9 healthy	15 g/day	Citrus pectin	−13	3
20 hypercholesterolemic	57 g/day	Pectin-EC[a]	−3.2 (NS)	6
12 normal	12 g/day	Pectin	−9	3
21 normal	15 g/day	Pectin	−8.6	6
7 normal	36 g/day	Pectin	−12	2
9 normal	15 g/day	Pectin	−15	3
18 normal	10 g/day	Pectin	−5	4
13 hyperlipidemic	6 g/day	HMP (apple)	7.5 (NS)	6
10 hyperlipidemic	6 g/day	HMP (lemon)	−8 (NS)	6
10 normal	12 g/day	Pectin	NS	4
10 female	24 g/day	Citrus fiber	12 (NS)[b]	4

LMP, low-methoxyl pectin; HMP, high-methoxyl pectin; NS, nonsignificant.
[a] Enriched cereal.
[b] Nonsignificant for LDL—only HDL cholesterol was reduced.

Table 6 and 7 – Tables showing the reductions in cholesterol levels after administration of pectin to different animal species (Fernandez, 2001).

Reduction in LDL plasma concentrations – Pectin has shown to play a role in reducing LDL plasma concentrations. LDL cholesterol is the undesirable form of cholesterol, and leads to coronary heart disease and artherosclerosis. There are several hypotheses as to why this is the case. Most scientists agree that part of the reason pectin reduces LDL levels is that it reduces the amount of fat that can be absorbed into the intestinal walls by absorbing water from ingested food, and also by thickening the lining of the intestines. However, other than this aspect, scientists diverge on their explanations of how the pectin reduces LDL plasma concentrations. Some scientists believe that pectin reduces the stability of the micelles that are formed in the intestine, and which are necessary for successful absorption of fatty acids. This occurs when the pectin coats the micelles, keeping them from holding

together by causing electrostatic repulsion between the micelles. Other scientists believe that pectin works by keeping bile acids from breaking down ingested fatty acids into the smaller pieces required for digestion and absorption into the intestinal wall. Whatever the mechanism, studies consistently show a high correlation between pectin consumption and reduction in LDL cholesterol. **Table 6** and **Table 7** are tables that show reduction in cholesterol levels due to administering of pectin to various animal (**Table 6**) and humans of different health conditions (**Table 7**).

Glycemic Control – Insulin-dependent and type II diabetic patients have exhibited a positive response to pectin consumption. Normally after consuming carbohydrates, blood glucose levels rise. In people with diabetes this is an issue, and can lead to serious consequences if not controlled through diet and/or medication. In several studies, patients that consumed pectin exhibited more controlled rises in glucose levels. The scientists determined that this was due to the viscosity of the consumed fiber, pectin being a source of soluble fiber. Essentially, the pectin latch on to the food molecules and slow down their progression through the body. Further, since pectin is only broken down by enzymes in the colon, and not by any of the enzymes excreted by the stomach or pancreas, fewer of the food molecules are absorbed into the body, so fewer food molecules are available to raise glucose levels in the blood. In particular, the prickly pear has shown to have positive effects on blood glucose levels. Finally, studies suggest that pectin can thicken the lining in the intestine, making it harder for food molecules to be absorbed into the intestine. This further inhibits a rise in glucose levels (Fernandez, 2001).

Reducing and Preventing Cancer - Many recent studies are showing that administering pectin could reduce the risk of cancer, or even halt the progression of cancer(Iurisci, et al., 2009) (Gunning, Bongaerts, & Morris, 2009). In the case of one study, administering pectin to cancer cells inhibited the growth of new cancer cells, and in a certain percentage of cases caused the cancer cells to start to die (Iurisci, et al., 2009). If this can be developed further, pectin administration could be a good co-treatment for chemotherapy or radiation, possibly allowing for a reduction in the amount of chemotherapy or radiation required.

This would be a positive advancement, due to the high toxicity to the body of both chemotherapy and radiation.

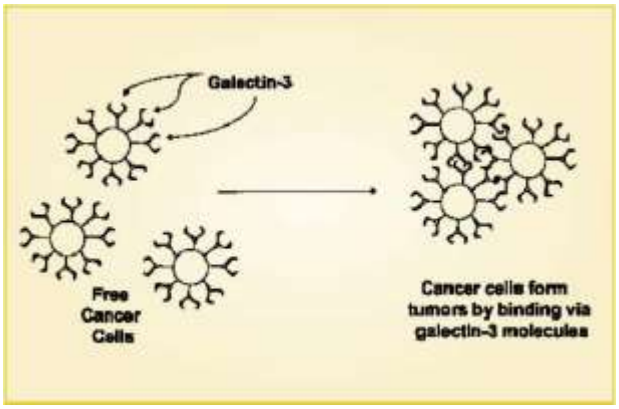

Fig. 18 – A schematic of the clumping of galectin-3, which can lead to the growth of cancer cells (Fox, 2004)

The bulk of the studies that address pectin and cancer center around its apparent ability to bond with a particular protein called galectin-3. Galectin-3 is a protein that has been recognized as a cancer-causing agent. What happens is the galectin-3 molecules start to bond together (see **Fig 18**). Once they bond together, cancer cells start forming as a result of the clumped proteins. When pectin is administered, the pectin bonds to the individual galectin-3 molecules, inhibiting clumping. The galectin-3 then passes out of the body, with the pectin (Gunning, Bongaerts, & Morris, 2009).

Future of Pectin

So what is the future of this miracle molecules? Well, in this time of increasing awareness of global warming and greenhouse gasses, some scientists have been looking at the methane emissions that could occur from the breakdown of pectin chains (Messenger, McLeod, & Fry, 2009). Since HM pectin has a high number of methyl-esterified GalA units, and the process of de-esterification removes the methyl group, and considering our consumption of pectin is growing so rapidly, this may warrant more examination.

Another area that scientists are just beginning to examine centers around changing the plant molecule inside the plant, before extraction. Studies involving the suppression of genes related to the development of polygalacturonase, as well as genetic manipulation of the development of the pectin side chains has been conducted in laboratories with some success. This latter research could lead to being able to use other materials in pectin manufacture, that might not have been useable before, due to having undesirable pectin conformations (Willats, Knox, & Mikkelsen, 2006).

Either way, whether science is looking at ways it is harming our environment, or improving our health and way of living, we will surely be uncovering more reasons that pectin is a miracle molecule, and that an apple a day may, very well, keep the doctor away.

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