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# Pectin as a bioactive polysaccharide – Extracting tailored function from less

Louise Wicker [a,b,*], Yookyung Kim [b], Mi-Ja Kim [c], Brittnee Thirkield [a], Zhuangsheng Lin [a], Jiyoung Jung [a]

[a] Department of Food Science and Technology, University of Georgia, Athens, GA, USA
[b] Department of Home Economics Education, College of Education, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-701, South Korea
[c] The Institute of Life Science, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-Gu, Gyeonggi-do, 440-746 Suwon, South Korea

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ABSTRACT

Pectin is a complex structural polysaccharide located in the cell wall and middle lamella of higher plants. The homogalacturon (HG) regions may be methyl esterified or de-esterified to create a block co-polymer structure. The HG backbone may be interrupted by neutral sugar side chains forming the rhamnogalacturon I (RGI) region, or rhamnogalacturon II (RGII), a conserved structure. In addition, protein, ferulic acid and acetyl groups may be found on some sources of pectin. While pectin has positive health effects against many diseases related to inflammation and as a delivery vehicle for bioactives for colon targeted delivery, conflicting results are reported and may be related to paucity of physico-chemical information or source of pectin. Pectin structure can be enzymatically or chemically modified to produce molecular fragments that can be used to successfully entrap phytochemicals for emulsion based targeted delivery to the colon. Likewise, charge modified pectin allows the development of delivery systems based on hydrogel technology. Pectin is recognized as a soluble dietary fiber, and likely has multiple outcomes against cardiovascular disease. More recent evidence also points to the role of neutral sugars, arabino-oligosaccharides, and ferulic acid and other phenolics associated with pectin as a dietary fiber and *in vitro* fermentability of selected domains of pectin and associated colonic metabolites on inflammation and gut health. While the mechanism of the positive effects of pectin remain to be elucidated, emerging evidence points to synergism between specific domains of pectin structure and other food constituents.


## 1. Introduction

A major trend in the food industry is development of convenient fruit and vegetable based food products and use of naturally sourced ingredients. As a ubiquitous component of fruits and vegetables, pectin is a major contributor to textural quality of fruit and vegetable products and is typically used as a gelling agent in jams, jellies and confections. Also, pectin is an effective stabilizer in colloidal dispersions ranging from emulsions, juice blended drinks, high protein fruit drinks, to anti-oxidant fortified foods. Pectin and other sources of dietary fiber are associated with gastrointestinal health, reduced risk of some cancers, glucose tolerance, lipid digestion and weight management (Dikeman & Fahey, 2006); current recommended fiber intake is 36 g fiber/2500 calorie diet (Lattimer & Haub, 2010). This amount of added fiber or fiber naturally present in foods adversely affects the palatability of foods and gastrointestinal tolerance for many individuals. Actual fiber consumption is about half the recommended amount (Clemens et al., 2012). Fruit and vegetable food products, rich in fiber, must also taste good and appeal to the consumer.

The ability to relate structural information to technical performance provides foundational knowledge for product developers in the food industry to use tailored pectins for specific applications for healthier foods. This review summarizes knowledge that relates specific structural domains of pectin to selected health benefits. In a review of the nutrition literature, much of the beneficial effect attributed to pectin is reported without adequate characterization of pectin; discrepancies are often reported and results are difficult to compare. In addition, fiber is typically identified by solubility, but identification by physiological function and structural domains that contribute to function may be more useful. Finally, the synergistic effect between syn-, pre- and pro-biotics and gut health is being realized.

The reader is referred to some excellent recent reviews on the role of pectin as an anti-cancer treatment (Maxwell, Belshaw, Waldron, & Morris, 2012; Nangia-Makker et al., 2002; Wong,

* Corresponding author. Department of Food Science and Technology, University of Georgia, Athens, GA, USA.
*E-mail addresses:* lwicker@uga.edu (L. Wicker), mijakim71@nate.com (M.-J. Kim).

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Chan, Lee, & Heng, 2002; Wong, Colombo, & Sonvico, 2011). The Maxwell and Nangia-Makker reviews cover many aspects of cancer galectin-3 recognition and possible mechanisms of inhibition by pectin. The Wong et al. review deals primarily with pectin matrix for oral drugs, and the authors include a comprehensive overview of the development of colon cancer, colon anatomy and physiology, including physical dimensions, pH transitions through the GI system, colon cancer and pectin to moderate pH, GTT, enzyme activity, bile acid excretion, and fermentation and production of beneficial short chain fatty acids. The review included a precise summary of typical response differences between healthy and cancer patients. As is typical of many reviews on pectin and cancer development, there is a paucity of information on the structural nature of the pectin used in the many studies. The Maxwell et al. (2012) review is an excellent exception, which describes current knowledge relating specific structural features of pectin to ligand binding and specific anti-cancer effects.

Pectin is a complex hetero-polysaccharide, present in the middle lamella and primary cell wall of plants. Galacturonic acid (GalA) (α 1-4 linked) forms the homogalacturon (HG) backbone or smooth regions and may be methyl esterified. Rhamnogalacturonan (RGI) or hairy regions consists of 1,4 linked D GalA and 1,2 linked α L rhamnose, substituted with neutral sugars. Commercially extracted pectins are typically rich in the HG region, and depending on degree of esterification, may be used to make high or low sugar jellies and used as a stabilizer in a variety of food products. Commercial pectins vary according to average molecular weight and distribution, average total charge and distribution, neutral sugar side chains, degree of acetylation, ferulic acid presence, and protein presence. The RGI region is the primary site for attachment for neutral sugars (galactose, arabinose, glucose, other sugars) and linkages tend to be acid labile, alkaline stable. Other potential side chains include xylogalacturons, rich in reproductive tissue and seeds, and arabinogalactan I and II, mainly associated with protein. A number of the models to describe pectin in plants are described (Voragen, Coenen, Verhoef, & Schols, 2009; Yapo, 2011). Commercial extraction of pectin typically relies on acidic hydrolysis (nitric, sulfuric, hydrochloric, citric), at high temperatures (60–90 C) for extended times (1–6 h), followed by alcohol precipitation to recover primarily pectin. Laboratory extraction of pectin usually begins with precipitation of alcohol insoluble solids, to remove simple sugars and sequential extraction in buffers to fractionate water soluble, chelator soluble, acid soluble and alkali soluble pectin. While yield is low without acidic hydrolysis, neutral sugar side chains and other substituents are better preserved (Vierhuis, Schols, Beldman, & Voragen, 2000). In pectin extracted from different sources or by novel extraction techniques, such as microwave assisted extraction, higher structural domains are observed that include rod like and branched, compact spherical structures (Fishman, Cooke, Chau, Coffin, & Hotchkiss, 2007).

The body of work on pectin as a bioactive polysaccharide is extensive and this review does not attempt to summarize the entirety. As noted in a review (Brownlee, 2011) on the physiological role of fiber, there are some consistencies in the literature on fiber and health, notably the influence of pectin on gut transit time. However, there are vast differences in findings in the literature, which are likely related to methodology and consistency of source material, which hamper interpretation of results. The present review summarizes knowledge that relates specific structural domains of pectin to selected health benefits. In addition, fiber is typically identified by solubility, but identification by physiological function and structural domains that contribute to function is emerging as a defining criterion. Finally, the synergistic effects between syn-, pre- and pro-biotics and gut health are being realized. If indeed, only domains of the complex structure of pectin have specific bioactivity, perhaps pectin fractions can be tailored for use in foods at lower amounts, which are still highly effective in promoting health. This work summarizes recent literature that documents structural domains of pectin, synergism with synbiotics and potential gut health. This contribution focuses on structural domains of pectin and potential effect on colonic health.

## 2. Pectin as emulsifier

Small amphiphilic molecules and proteins are more typically associated with emulsifying activity, but hydrocolloids also show emulsifying activity. Even though the mechanism for emulsifying activity has been attributed to small amounts of protein (Dickinson, 2003) or a specific interaction with the hydrocolloid moiety (Garti & Leser, 2001), it is clear that like gum acacia, sugar beet pectin (SBP) has strong emulsifying activity. In practice, hydrocolloids like pectin are typically used in conjunction with another emulsifying agent such as β-lactoglobulin, either as a complex or in a layer by layer deposition on the oil interface, recently reviewed (McClements, Decker, Park, & Weiss, 2009). The bioactivity of SBP derives from the emulsifying activity of pectin and potential to encapsulate and to protect bioactives for delivery to targeted sites. The structural basis for the emulsifying activity of SBP is reported, but there is an incomplete understanding of the structural contribution to emulsifying activity. Further, there is still very little data on the application of SBP, in the absence of other amphiphiles such as proteins, with loaded emulsions. SBP was used to encapsulate fish oil with a high efficiency, near 50% oil, and 2.2% SBP and high stability (Drusch, 2007; Drusch, Serfert, Scampicchio, Schmidt-Hansberg, & Schwarz, 2007). Encapsulation efficiency of 90% for fish oil was reported but the capsule was prone to accelerated lipid oxidation attributed to residual metal ions (Polavarapu, Oliver, Ajlouni, & Augustin, 2012).

SBP is unique among commercial pectins in that it has poor gelling properties, attributed to acetylation and pectin contains ferulic acid (Levigne, Ralet, & Thibault, 2002). Compared to other commercial sources of pectin, SBP also has a greater amount of protein that varies depending on source and extraction conditions; the amount ranges from about 2% (Leroux, Langendorff, Schick, Vaishnav, & Mazoyer, 2003) to more than 10% (Thibault, 1988). Like the protein moiety of other emulsifying hydrocolloids like gum acacia (Phillips, 1998) or xanthan (Garti et al., 1993), the contribution of the protein moiety in SBP to emulsifying activity is documented by several experimental approaches. The fraction of the pectin that forms stable emulsions is higher in protein (Akhtar, Dickinson, Mazoyer, & Langendorff, 2002; Leroux et al., 2003; Williams et al., 2005; Yapo, Robert, Etienne, Wathelet, & Paquot, 2007). Further, the SBP that adsorbs to the oil droplet interface is enriched in protein compared to bulk phase SBP (Akhtar et al., 2002; Funami et al., 2011; Leroux et al., 2003; Siew, Williams, Cui, & Wang, 2008).

Nevertheless, neither high protein concentration nor presence of protein ensures good emulsifying activity. SBP fractionated by hydrophobic chromatography differed widely in protein content and the elution profile did not coincide with emulsifying activity. While some fractions that were relatively high in protein had good emulsifying activity, at least one protein depleted fraction also had strong emulsifying activity, while one protein rich fraction had poor emulsifying activity (Williams et al., 2005). Poor correlation of protein content with emulsifying activity was observed in SBP extracted (Yapo, Robert, et al., 2007) and concentrated (Yapo, Wathelet, & Paquot, 2007) by different methods. Protease treatment of SBP reduced emulsifying activity (Funami et al., 2011; Siew et al., 2008). Hence, the literature is mixed on the relative contribution of protein to emulsifying activity.