Food Hydrocolloids xxx (2016) 1–8

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

# The production of galacturonic acid enriched fractions and their functionality

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ARTICLE INFO

*Article history:*
Received 14 July 2016
Received in revised form
18 November 2016
Accepted 21 November 2016
Available online xxx

*Keywords:*
Galacturonic acid oligosaccharides and polysaccharides
Thickening and gelling agent
Prebiotic
Physiological functions

ABSTRACT

Vegetable tissues discarded at harvesting or after industrial processing constitute a valuable and renewable source of biopolymers and bioactive compounds. Upgrading of vegetable waste can not only reduce pollution but also add value to the commodity production. Plant cell walls are an important source of galacturonic acid compounds The present paper reviews some selected bibliography published in the last years concerning the production of pectin and oligosaccharides based on galacturonic acid, and their functionality with special reference to their effect on health.

In relation to pectin it can be concluded that, in addition to their ability to thicken and form gels, they are soluble dietary fibers. They can also act as prebiotics, but more systematic studies must be performed to elucidate the effect of their chemical structure on health. With respect to pectic oligosaccharides rich in galacturonic acid, they have been proposed as prebiotics and immunity enhancers, but the absence of standardized techniques for their production and purification, the ample variety of substrates involved and the lack of systematic studies about their structure does not allow to conclude nowadays about the structure-function relationship and it is a must to deepen these studies to help to the rational usage of oligosaccharides in functional foods.



## 1. Introduction

Vegetable tissues discarded at harvesting or after industrial processing constitute a valuable and renewable source of biopolymers and bioactive compounds (Goñi & Hervert-Hernández, 2011).

Polymerized anhydrogalacturonic acid in which some of the carboxylic acid groups are methyl esterified is the main constituent of pectin (Nussinovitch, 1997) which can be isolated from plant tissues by means of disruption of cell wall and middle lamella. It is well known that pectin acts modifying food rheology and texture due to its thickening and gelling capacity (Kjøniksen, Hiorth, & Nystrom, 2005). Pectin is a soluble dietary fiber that has also direct and indirect nutritional and physiological actions (Dongowski, Lorenz, & Anger, 2000) in relation to human health.

Partial hydrolysis of pectin by chemical and/or enzymatic methods leads to the production of pectin-derived oligosaccharides (POS), which have been proposed as having important physiological properties, including their prebiotic activity (Mandalari et al., 2007; Mussatto & Mancilha, 2007).

The present paper reviews some selected bibliography published in the last years concerning the production and properties of pectin and oligosaccharides based on D-galacturonic acid, with the purpose of contributing to: a) systematizing the information, and b) the understanding of the effect of the different substrates used and the procedures followed for their production, on the functionality of these compounds.

## 2. Pectin

D-galacturonic is an acid sugar. It is a monosaccharide containing six carbon atoms and its structure corresponds to the oxidized form of galactose. In its open form, it has an aldehyde group at C1 and a carboxylic acid group at C6.

Polymerized anhydrogalacturonic acid in which some of the carboxylic acid groups are methyl esterified is the main constituent of pectin (Nussinovitch, 1997). The pectins are abundant in the primary cell walls and the middle lamellae of plants.

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http://dx.doi.org/10.1016/j.foodhyd.2016.11.030
0268-005X/

The structural classes of the pectic polysaccharides include homogalacturonan (HG), xylogalacturonan (XGA), apiogalacturonan (AGA), rhamnogalacturonan II (RG-II) and rhamnogalacturonan I (RG-I) (Caffall & Mohnen, 2009).

The HG, RG-I and RG-II domains can be covalently linked to form a pectic network throughout the primary cell wall matrix and middle lamellae. HG is a linear homopolymer of α-1,4-linked anhydrogalacturonic acid and is thought to contain some 100–200 galacturonic acic (GalA) residues and is present in the cell wall in a form that has 70–80% of GalA residues methylesterified at the C-6 carboxyl (Willats, McCartney, Mackie, & Knox, 2001) but esterification degree depends on plant species, plant tissues and ripeness state (Hyodo et al., 2013) and can be modified by isolation technique. The removal of methyl ester groups within the cell wall matrix results in HG capable of being cross-linked by calcium and form gels. GalA residues in HG can be O-acetylated, predominantly at C-3. The substitution of the C-3 of GalA with residues of xylose produces a domain known as xylogalacturonan. Substitution of GalA with apiose at C-2 or C-3 results in apiogalacturonan. RG-I is an acidic pectic domain consisting of as many as 100 repeats of the disaccharide α-1,2-L-rhamnose- α-1,4-D-galacturonic acid which has been isolated from a wide range of plants and is ramified principally with arabinan, galactan and arabinogalactan (Mohnen, 2008). RG-II is a branched pectic domain containing a backbone of around 9 GalA residues that are α-1,4-linked and is substituted by 4 heteropolymeric side chains that contain eleven different sugars including apiose, aceric acid and 2-keto-3-deoxy-D-manno-octulosonic acid (KDO) (Albersheim, Darvill, O'Neill, Scols, & Voragen, 1996; Willats et al., 2001; Gullon et al., 2013).

Pectin is present in an ample variety of plant tissues and can exert different actions. For example, Njoroge et al. (2014, 2015) reported the influence of its structure and cross-linking on the development of hard to cook behavior of common beans.

The main uses for pectins are as gelling agents, thickening agents and stabilizers in foods. Pectins have a great capacity for water retention and can gel under adequate conditions. The consumption of soluble polysaccharides which increase the viscosity can delay and reduce the concentration of glucose in blood because of the restricted access of amylases to starch. Soluble polysaccharides can also reduce the levels of total cholesterol and low density lipoproteins (LDL) cholesterol in blood (Brouns et al., 2012).

Emulsifying properties have been also reported and are attributed to the proteins that are associated to pectins (Saha & Bhattacharya, 2010; Ngouémazong, Christiaens, Shpigeman, Van Loey, & Hendrickx, 2015).

According to their degree of methylation, pectins can be classified as high methoxyl pectins, HMPs (50% esterified or higher) or low methoxyl pectins, LMPs (less than 50% esterified). HMPs form gels in acidic and high soluble solid conditions whereas LMPs gel in the presence of divalent ions such as calcium, being this capacity of great interest in low caloric value foods (Seshadri, Weiss, Hulbert, & Mount, 2003). For the high methoxyl pectins, chain association occurs by means of junction zones that are stabilized by hydrogen bonds between non-dissociated carboxyl and secondary alcohol groups and by hydrophobic interactions between methoxyl groups. This phenomena changes food viscosity and can produce gelation. It is well known that HMPs form gels at acid pH in presence of a large amount of sugars which reduce the water activity. For LMPs, hydrogen-bonded intermolecular complexes play a prominent role in the chain association process. For this type of pectins, the gelation occurs in the presence of divalent cations such as calcium, which act as a bridge between pairs of carboxyl groups of different pectin chains (Fraeye, Duvetter, Doungla, Van Loey, & Hendrix, 2010; Kjøniksen et al., 2005).

Carbohydrate polymers with ten or more monomeric units, which are not hydrolyzed by the endogenous enzymes in the small intestine of humans, are considered as dietary fiber compounds (Philips & Cui, 2011). This definition can be extended to carbohydrate polymers with three to nine monomers (Lupton, Betteridge, Loek, & Pijls, 2009). Non-processed carbohydrates transit the large intestine where they become food for the commensal bacterial community. The species within the gut microbiota use a variety of strategies to process and scavenge both dietary and host-produced carbohydrates such as mucins. They produce secondary metabolites and fermentation derived compounds that can influence cell proliferation and apoptosis, modulate the immune response and can alter host metabolism impacting on obesity, diabetes, inflammatory bowel disease, colon cancer, gastrointestinal infections, and potentially many health problems (Cockburn & Koropatkin, 2016).

Pectins are a type of soluble fiber commonly present in vegetal tissues, and this review will focus on innovative methods proposed for their isolation, on the use of non-traditional substrates for their production and on the functional properties they have in relation to health.

### 2.1. Isolation of pectins

The biopolymer network present in plant tissues must be partially disrupted to enable extraction of pectin, for example, through the use of calcium-chelating agents, alkali or acid. Extraction conditions can alter pectin composition, structure and physiological properties. Pectin extraction from raw material is usually performed on citric peels or apple bagasse remaining from industrialization of these fruits, under acidic conditions (pH 1.5–3.0) and at high temperatures (70–90 °C) using hydrochloric acid, nitric acid or sulfuric acid. The raw acid extract is separated, in general, from the residue by filtration or centrifugation and pectin is precipitated with alcohol. Purification, drying and milling yield powdered pectin (Vriesmann, Teófilo, & de Oliveira Petkowicz, 2011).

The acidic conditions generally used by the industry generate a high amount of effluents and their treatment represents an additional cost that promotes the development of more environmentally friendly procedures.

The use of non pectolytic enzymes for pectin extraction is an alternative to industrial acidic extraction. These enzymatic techniques have been described by different authors. For example, Ptichkina, Markina, and Rumyantseva (2008) obtained pectin from an alternative source such as pumpkin (*Volzhskaya Grey* variety) using cellulase and pectinesterase activities. Fissore, Matkovic, Wider, Rojas, and Gerschenson (2009), Fissore, Ponce et al. (2009), and Fissore et al. (2011) studied the isolation of butternut (*Cucurbita moschata*) and red beet (*Beta vulgaris)* pectin by means of the use of cellulase and hemicellulase activities. Campbell (2006) studied the optimized production of pectin form watermelon (*Citrullus lanatus*) using cellulase. A more detailed explanation of these researches is given in Table 1.

Other authors studied the pectin extraction with the help of different techniques. For example, Chen, Hu, Yao, and Liang (2016) proposed the extraction from processed pomelo peels previously submitted to an essential oil extraction, with the help of microwaves and using hydrochloric acid (Table 1) observing a diminishing of processing time. Freitas de Oliveira et al. (2016) evaluated by response surface methodology, the effect of ultrasound power intensity and of the temperature used, on the pectin extraction from passion fruit peel using nitric acid and concluded that ultrasound increased pectin yield (Table 1). Pereira et al. (2016) studied the extraction of pectins from pomegranate peels with citric acid, a more environmentally friendly acid (Table 1).

Please cite this article in press as: Gerschenson, L. N., The production of galacturonic acid enriched fractions and their functionality, *Food Hydrocolloids* (2016), http://dx.doi.org/10.1016/j.foodhyd.2016.11.030