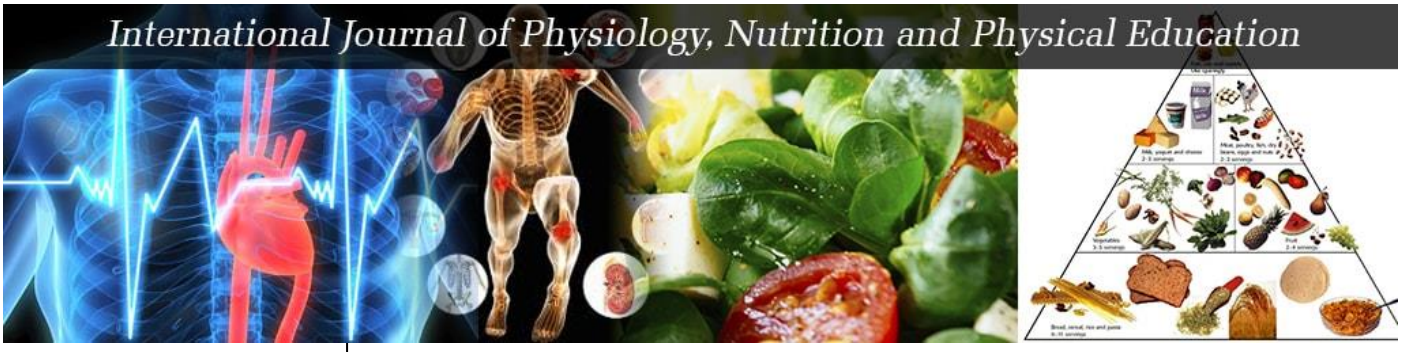

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Pectins: Structurally versatile polysaccharides with immense biological activities

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Abstract
Pectins or pectic polysaccharides belong to the class of structurally complex polysaccharides that are one of the major components of plant primary cell wall. Based on structural features, pectic polysaccharides may be divided into three categories such as: homogalaturonans (HG), rhamnogalacturonan I (RG-I), and rhamnogalacturonan II (RG-II). Galacturonic acid is the main constituent of pectins. Pectin allows primary cell wall extension and growth of plants. It is a natural part of the human diet, but does not contribute significantly to nutrition. In human digestion, pectin binds to cholesterol in the gastrointestinal tract and slows down glucose absorption by tapping carbohydrates. Pectin is thus a soluble dietary fiber. Consumption of pectin has been shown to reduce blood cholesterol levels. In the large intestine and colon, microorganism degraded pectin and liberates short- chain fatty acids. In this way pectins exhibit prebiotic effect. The association of pectin chains leads to the formation of the three dimensional networks that is to gel formation.The pectin, by itself or by its gelling properties, was employed in pharmaceutical industry, health promotion and treatment. Pectin's have been utilized for their functionality in foods for many years. This review will discuss the importance of pectin and its chemistry, general properties of pectin, and its biological activities.

Keywords: Pectic polysaccharides, immune system, prebiotic effect, antitumor and anti metastasis activities

1. Introduction
Pectin was first isolated and described in 1825 by Henri Braconnot [1], although the action of pectin to make jams and marmalades was known from long before. Pectin rich fruits or their extracts were mixed into the recipe to obtain well set jams. In the beginning of the 12th century, factories were built in USA and Europe to commercially extract pectin from dried apple pomace and citrus peel. Since that time pectin has been used for its gel formation, thickening and stabilizing properties in the wide range of application from food to the pharmaceutical and cosmetic industries. The amount, structure and chemical composition of pectin differs among plants, within a plant over time, and in various part of a plant. During fruit ripening, pectin is broken down by the enzymes pectinase and pectinesterase, in which process the fruit becomes softer as the middle lamellae break down and cells become separated from each other [2]. Pectic polysaccharides are generally divided into three types depending on structural features: homogalaturonans (HG), rhamnogalacturonan I (RG-I), and rhamnogalacturonan II (RG-II) [3]. Galacturonic acid is the main constituent of pectins. In nature, about 80% of carboxyl groups of galacturonic acid are esterified [4]. The non-esterified galacturonic acid units can either be free acids (carboxyl groups) or salts with sodium. potassium or calcium. Sometimes the galacturonic acid is converted with ammonia to carboxylic acid amide which is known as amidated pectin. The side chains and acetyl groups of galacturonic acid may play important bioactive roles [5]. Structural diversity of pectin is related to the status of cell proliferation and cell differentiation and production of nitric oxide (NO) which is an important mediator molecule, implicated in various biological processes, such as circulatory regulation, nervous signal transduction, immune defence and tumorigenesis [6].

2. Structural features of pectin
The main role of cell-wall polymers is related to cell expansion and mechanical strength. The

components of cell-wall include cellulose, hemicelluloses and pectins. Cellulose microfibrils are coated with hemicelluloses and immersed in a pectic matrix also containing cell-wall proteins such as extension. When a cell grows, the bonds between existing wall polysaccharides are broken and, as the wall expands, newly synthesized wall polysaccharides are inserted between existing ones. This process undoubtedly involves the breaking and formation of numerous covalent and non-covalent bonds. In this way, cells can elongate many times length without weakening the wall. The 2nd major function of pectin is associated with plant defense through the release of signaling molecules or oligosaccharides (about 10 to 15 residues of short sequences of α-(1→4)-linked-D-galacturonic acid) from the wall upon attack by various pathogens.

Pectin is defined as hetero-polysaccharide predominantly containing galacturonic acid (GalA) residues, in which varying proportions of the acid groups are present as methoxyl esters, while a certain amount of neutral sugars might be present as side chains [7]. De Vries [8] recognized a pattern of ‘‘smooth’’ homogalacturonic regions and ramified ‘‘hairy’’ regions, in which most of the neutral sugars are located. Over the years many pectin structural elements have been described and all pectins are believed to essentially contain the same repeating elements, although the amount and chemical fine structure of these elements varies [9–11].

2.1 Homogalacturonan (HG)

Homogalacturonan (HG) is the major type of pectin in cell walls, accounting for approximately 60% of the total pectin amount [12, 13]. The HG polymer consists of a backbone of α-(1→4)-linked D-GalA residues [14]. The minimum estimated length of this backbone is, for citrus, sugar beet, and apple pectin 72–100 GalA residues [15]. GalA moieties within this backbone may be methyl esterified at C-6 [16, 17] and/ or O-acetylated at O-2 and/or O-3 [18, 19]. The molecule is classified according to its esterification level: pectin has least 75% of the carboxyl groups methylated; pectinic acid has less than 75% of the carboxyl groups methylated; pectic acid or polygalacturonic acid has no methyl esterified carboxyl groups. However, not only the amount of methyl-esterification is important, but also the distribution of these esters is. The suggestion made by Rees and Wight [20] that HG elements could be interspersed with single L-rhamnose residues, resulting in a kink of the molecule, was convincingly argued against by Zhan *et al*. [21].

2.2 Rhamnogalacturonan I (RG-I)

Rhamnogalacturonan I pectins (RG-I) contain a backbone of the repeating disaccharide →4)- α- D-galacturonic acid-(1→2)- α-L-rhamnose-(1→. From many of the rhamnose residues, side chains of various neutral sugars branch off. The neutral sugars are mainly D-galactose, L-arabinose and D-xylose. The rhamnosyl residues of RGI can be substituted at O-4 with neutral sugars side chains [22, 23, 24]. These side chains are mainly composed of galactosyl and/or arabinosyl residues. Both single unit [b-D-Galp-(1→4)] as well as polymeric substitutions, such as arabinogalactan I (AGI) and arabinan (50 glycosyl residues or more) have been identified [23, 25] in the side chains. The proportion of branched Rha residues varies from approx. 20% to approx. 80% depending on the source of the polysaccharide [20].

2.3 Rhamnogalacturonan II (RG-II)

Rhamnogalacturonan II (RGII) is a highly conserved structure in the plant kingdom and can be released by endo-polygalacturonase action. Rhamnogalacturonan II is classified by some authors within the group of substituted galacturonans since the Rhamnogalacturonan II backbone is made exclusively of D- GalA units. The structure is characterized as a distinct region within HG, containing clusters of four different side chains with very peculiar sugar residues, such as apiose, aceric acid, 3deoxy-lyxo-2-heptulosaric acid (DHA), and 3-deoxy-manno-2-octulosonic acid (KDO). These side chains are attached to a HG fragment of approximately nine GalA residues, of which some are methyl-esterified [26, 27, 28]. Isolated pecdtin has a molecular weight of typically 60-130,000 g/mol, varying with origin and extraction conditions.

In low-ester pectins, ionic bridges are formed between calcium ions and the ionized carboxyl groups of the galacturonic acid. This is idealized in the so-called “egg box-model” [29]. Low-ester pectins need calcium to form gel, but can do so at lower soluble solids and higher pH-values than high-ester pectins. High-ester pectins set at higher temperatures than low ester pectins. However, gelling reactions with calcium are increased as the degree of esterification falls.

3. Structure Activity Relationship

The HG has linear chains of →4)-linked D-GalA residues. RG-I consists of alternating sequences of Rha and GalA, with side chains at Rha moieties. RG-II consists of alternating sequences of Rha and GalA, with side chains at both Rha and GalA moitries. The side chains and acetyl groups on GalA may play an important role in bioactivities. Pectic polysaccharides isolated from *B. petersianum* (BP100 III) have potent complement fixating activities [30]. There is a positive correlation between a high complement fixing activity and B cell proliferating activity. Arabinogalactan containing compoundsare known to be potent immune mopdulators, and arabinogalactan side chains are taught to be the site of biological activity in pectic polysaccharides. Pectic polysaccharide fractions oisolated from G. oppositifolius containing RG-II like structures showed no activity in the complement fixation test, B-cell proliferation assay, or macrophage activation, as opposed to fractions containing RG-I like structures [31]. However, pectic fractions containg RG-II structures isolated from other plants have been reported to have biological activity.

4. Biological activities

Pectin is increasingly recognised as an important precursor of substrates improving gastrointestinal functions. It plays an important role in the regulation of some physiological progresses and therefore it prevent of hyperlipidemia, as well as bowel cancer also [32]. It can protect leucocytes and lymphocytes of mice against radiation-induced damage, which has potential radio protective effect on acute radiation injured mice. Ginseng pectin inhibit adhesion of bacteria to host cells [33], protect animals from the lethal effects of ionizing radiation, reduce blood sugar in normal and hyperglycaemic mice [34] and also inhibit tumor growth and metastasis [35]. Consumption of pectin has been shown to reduce blood cholesterol levels. The mechanism appears to be an increase of viscosity in the intestinal tract, leading to a reduced absorption of cholesterol from bile or food. In the large intestine and colon, microorganisms degraded protein and liberated short-chain fatty acids that have positive influence on health.

5. Some other applications

Pectin is a natural part of the human diet, but does not significantly contribute to nutrition. In human digestion, pectin bind to cholesterol in the gastrointestinal tract and slows down glucose absorption by tapping carbohydrates [36]. Pectin is thus a soluble dietary fiber. Due to its large water binding capacity, pectin gives a feeling of satiety, thus reducing food consumption. Experiments showed a prolongation of the gastric emptying half-time from 23 to 50 minutes of a meal fortified with pectin [37]. These attributes of pectin are used in the treatment of disorders related to overeating [38]. Recently, Sungthongjeen [39] have investigated HM-pectins for their potential value in controlled release matrix formulations. Pectin beads prepared by the ionotropic gelation method [40] were used as a sustained release drug delivery system. However, the use of these beads has some drawbacks due to their rapid *in-vitro* release. An insoluble and uniform coating of calcium pectinate gel was formed around the pellets. The potential of pectin or its salt as a carrier for colonic drug delivery was first demonstrated by two studies, i.e. Ashford and Rubinstein, [41, 42]. The rationale for this is that pectin and calcium pectinate will be degraded by colonic pectinolytic enzymes [43], but will retard drug release in the upper gastrointestinal tract due to its insolubility and because it is not degraded by gastric or intestinal enzymes [44]. In medicine, pectin increases viscocity and volume of stool so that it may be used against constipation and diarrhoea. Pectins is also used in wound healing preparations and specialty medical adhesives, such ascolostomy devices. In the cigar industry, pectin is considered an excellent substitute for vegetable glue.

6. Conclusion

The chemistry and gel-forming characteristics of pectin have enabled this naturally occurring biopolymer to be used in pharmaceutical industry, health promotion and treatment. It has also been used potentially in pharmaceutical preparation and drug formulation as a carrier of a wide variety of biologically active agents, not only for sustained release applications but also as a carrier for targeting drugs to the colon for either local treatment or systemic action. As research and development continues with delivery system using pectin, we expect to see many innovative and exciting applications in the future.

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