Pectins and Olive Pectins

Subjects: Biology
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Pectins are a component of the complex heteropolysaccharide mixture present in the cell wall of higher plants. Structurally, the pectin backbone includes galacturonic acid to which neutral sugars are attached, resulting in functional regions in which the esterification of residues is crucial. Pectins influence many physiological processes in plants and are used industrially for both food and non-food applications. Pectin-based compounds are also a promising natural source of health-beneficial bioactive molecules. Olives, the fruit of the olive tree, are consumed as part of the healthy Mediterranean diet or processed into olive oil. Pectins from olives have recently emerged as promising compounds with health-beneficial effects.

Keywords: pectin ; polysaccharide ; galacturonic acid ; cell wall ; by-products ; bioactivity ; olive

1. Introduction

Pectins are present in the primary cell walls and middle lamellae in higher plants within a complex heteropolysaccharide matrix, which contains up to 30% pectins together with cellulose and hemicellulose [1][2] resulting in networks due to linkages among them. Carbohydrates are the major components of the cell wall, which contain only 5–10% of proteins, including extensins and arabinogalactan proteins [3][4]; all are modified during fruit ripening. Despite the diversity of their chemical composition across species and tissues, pectins are known to play a key role in plant tissue firmness and plant development, modulating the properties of the cell wall and cell functions. In plant tissues, pectins in the middle lamella also contribute to cell-to-cell adhesion and act as a barrier against pathogens [3][5][6]. Many studies have also highlighted the interaction between pectin chains and the cellulose-hemicellulose network [1][4][7][8][9][10][11][12][13].

Pectin polysaccharides have been extensively used as a functional ingredient in the food industry and also in non-food industries during the production of cosmetics, packaging materials or pharmaceuticals. Over the last few years, several studies point to an increasing interest in pectins as health-promoting molecules for biomedical applications. Nevertheless, it is well established that pectin extraction methods strongly influence the structure and properties of these polysaccharides [1][14]. This review summarizes current knowledge concerning pectin sources and extraction protocols. Additionally, we provide evidence that olive fruits may be a promising natural source of bioactive pectic polysaccharides obtained during olive oil production, which also valorize traditional industrial by-products or wastes.

2. Structure, Quantification, and Qualification

2.1. Pectins

Pectins are complex heteropolysaccharides, which include at least 17 kinds of monosaccharides and over 20 types of linkages, with a backbone of α-1,4-D-galacturonic acid (70%) in which homogalacturonan (HG), rhamnogalacturonan (RG-I and RG-II), and xylogalacturonan (XG) domains, linked by covalent or ionic interactions, can be distinguished [14][15]. Homogalacturonan linear domain monosaccharides are partially C-6 methyl-esterified and may be C-2/3 O-acetylated in some plant sources, and the degree of esterification is a parameter that affects pectin functionality [16]. This “smooth region” of HG is the most abundant pectin domain (comprising 60–65%) in plant cell pectins [15] and has been recently related to epidermal morphogenesis in plants [17]. The “hairy” regions of pectin molecules include both RG-I and RG-II, to which nonionic side chains containing many neutral sugars are attached [18]. RG-I domains include rhamnose residues in the galacturonic acid backbone with many side chains containing other neutral sugars, such as galactose or arabinose [8]. It is well established that the monosaccharide composition and architecture of both HG and RG-I domains vary significantly during plant development [19]. Only little structure variations in pectin RG-I domains have been reported in different plants [20]. RG-II is a much more complex domain, in which up to 12 types of sugar may be present, including the rarely observed apiose, xylose, or fucose [20].

2.2. Olive Pectins

The industrial production of olive oil generates huge quantities of a wet organic matter commonly known as olive pomace, composed of 60–70% water and containing 98% of the total phenols in the olive fruit, known for their beneficial properties for health [21]. Pectic polysaccharides comprise approximately 39% of this wet olive pomace. The degree of methyl esterification is approximately 48% and the degree of acetylation is approximately 11%. Compared to citrus commercially available low-methoxyl-pectins, olive pomace pectin extracts show a higher degree of methyl-esterification, acetylation, and total neutral sugar content, but a lower galacturonic acid percentage or molecular weight [21]. The presence of arabinan-rich pectic polysaccharides in olive pomace is notable, and its quantification is a parameter to evaluate the ripeness of the olive fruits [21]. These agricultural wastes therefore appear to be an interesting source of health-beneficial biomolecules that can be recovered to yield environmental and economic benefits [22].

3. Extraction

3.1. Pectins

From the raw biomass, the industrial process of extraction requires pre-extraction protocols, followed by hydrolysis and isolation of pectins and post-extraction solubilization.

Both single digestions and combined methods have been used extensively for pectin extraction [1][14][20][23]. Single extraction methods use acid or alkali solutions in addition to enzyme treatments to release pectins from the cell wall, where it forms complex networks with cellulose and hemicellulose.

Pulsed electric field extraction or the use of hot water or chelating agents, such as oxalate or sodium hexametaphosphate, are also single extraction methods [1][24]. A pulsed electric field applies a high voltage during a short time to a food product, increasing cell membrane permeability and facilitating bioactive molecules release [24]. Nevertheless, these protocols are time- and energy-consuming, with low extraction yields and inadequate pectin quality or functionality, as well as environmental disadvantages due to contaminants generated [14][25]. However, the structure and properties of pectins are influenced by the extraction method; thus, there is a need to find novel extraction techniques that achieve the optimal yield and quality of the by-products generated and the isolated pectic polysaccharide products [23]. Accordingly, combined techniques using subcritical water-, ultrasound-, microwave-, or ultrasonic/microwave-assisted protocols are promising approaches for pectin extraction [1].

3.2. Olive Pectins

At present, two-phase extraction is preferred in the olive oil industry as it reduces the consumption of water and the generation of liquid pollution. The resulting solid phase includes water and vegetable mass and is commonly known as "wet olive pomace" [26][21]. Pectins are minor compounds in the olive fruit but comprise up to 35% of the olive pomace during processing [22][21], depending on the ripening stage and other factors related to cultivar conditions and olive variety [27][28][29].

Pectins can be extracted from olive pomace as an "alcohol-insoluble residue" (AIR), which also includes additional cell wall materials such as cellulose, hemicellulose or proteins [27]. Conventional methods already described, such as high temperature or acid solvents, have been used extensively in extraction protocols [28][30][31]. Some data point to low molecular weight pectins as bioactive compounds and, accordingly, hydrothermal treatment has appeared as a promising technology for the production and solubilization of pectins from olive pomace, as temperature is a critical parameter for maintaining the bioactivity of pectin [32][33]. Regarding the million tons of olive pomace produced every year by the olive oil industry, this by-product appears to be a noteworthy source of bioactive molecules, including pectic polysaccharides.

4. Industrial Applications

4.1. Pectins

Pectins have been used historically as additives in the food industry, including gelling, emulsifying, and stabilizing agents, as well as texture or thickness modulators, and fat-replacing components [18][34]. They have good biocompatibility and biodegradability, lack toxicity, and contribute to our dietary soluble fibers as no enzymatic digestion pectins occur in the human upper gut [18]. Nevertheless, some properties of pectins are strongly influenced by the number and localization of the esterified residues in the homogalacturonan region of the molecule [8]. Consequently, high-methylesterified (HM, 60–80%) and low-methylesterified (LM, 30–40%) pectins are suitable gelling agents for various products. Vegetable jellies include LM pectins, whereas other jellies, marmalade, mayonnaise, juices, or canned fish include HM pectins, which are more suitable for gelation [18][35].

The properties of pectins are also used in non-food industries, such as the pharmaceutical or cosmetics industry. As an emulsifier or thickening agent, pectins are present in cosmetic products and they are also useful as delivery vehicles for genes [31] or drugs [18][36][37][38]. Other industrial applications suggest that pectin-containing polymers are suitable for the preparation of biomaterials for various purposes [18].

4.2. Olive Pectins

Olive pomace polysaccharides have an 11% (acetyl)–48% (methyl) low degree of esterification, which points to the gelling potential as a food ingredient of this by-product in oil production [22]. What is more, in the presence of calcium, olive pomace pectins are able to form elastic gels more resistant to high temperatures than those commercial low-methoxyl-pectin/calcium gels [21]. The emulsifying activity of olive pomace polysaccharides has been proven compared with traditional sources of pectins [33].

5. Bioactivity

5.1. Pectins

New ventures to find natural sources of pectins in plants have the potential to expand what is known about vegetal polysaccharides as bioactive compounds that are available in large quantities but are still considered as waste. Many biomaterials are based on the pectin molecule, and many studies have assessed the efficiency of pectins as wound-healing agents [39] or in tissue engineering [18][40][41]. Pectins are a common dietary source of oligosaccharides from fruits and vegetables that are fermented in the colon by the gut microbiota. Promising activities include bactericidal, immunomodulatory, anti-inflammatory [42][43], antioxidant, cardioprotective, probiotic [44], cholesterol [45], serum glucose-reducing [46], and intestinal and obesity regulator [22][39][47] functions for pectin oligosaccharides. Moreover, low molecular weight fragments from pectins exhibit antitumoral activities [22][48][49][50][51][52]. Recent studies have also pointed to the importance of fruit and vegetables as an important source of pectin molecules containing the RG-I domain [19][53].

5.2. Olive Pectins

The chemical composition of olive fruits varies depending on the cultivar, environmental conditions, and the maturation from green to black fruits. Many studies have provided data concerning olive phenols [54], but despite the importance of pectin transformation in the cell wall, there is little published research on this topic [6][26][22][27].

As already stated, the olive pomace resulting from olive oil production has been described as a valuable source of olive pectins [21]. Given the economic and environmental relevance of olive cultivars and the increasing popularity of natural, bioactive, and healthy phytochemicals, olive pectin extracts are a potential new complement for both nutrition and health improvement that support research into the composition and distribution of olives [26].

Polysaccharide-enriched extracts from olive pomace have shown health-promoting activities in in vitro experiments, including those related to antioxidant behavior and the regulation of glucose or lipid metabolism compared with commercial pectins [33]. There are promising results demonstrating the antitumoral activity of pectin extracts from olive oil by-products [52].

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