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Pectin from low quality ‘Golden Delicious’ apples: Composition and gelling capability

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ABSTRACT

Pectin was acid-extracted from low quality ‘Golden Delicious’ apple fruit, yielding 16% (w pectin/w apple fruit). Composition and some of its physicochemical and functional properties were assessed. The pectin fraction presented a galacturonic acid content of 65% (w/w), an esterification degree of 57%, an intrinsic viscosity, [η], of 307 ml/g and a molecular weight (Mw) of 112 kDa. Pectin gels were obtained in 60% (w/v) fructose and pH 2.7. Pectin gels at 2.0% and 3.0% (w/v) presented hardness values of 10.2 and 20.4 g after 12 h at 4 °C. The gel hardness was greatly affected by aging (20% and 25% decrease in 48 h for gels at 2% and 3%, respectively). The results attained suggest the use of this gum as a potential texturing agent for the food industry.

1. Introduction

Pectin is a family of complex variable polysaccharides extracted from the primary cell wall of higher plants. Pectins are complex heteropolysaccharides consisting of homogalacturonan (“smooth”, α-(1→4)-linked partly methylesterified-D-*GalAp*-2-(1→2) units) and rhamnogalacturonan (“hairy”, GalA*p*-*a*-(1→2)-Rha*p*-α-(1→4)-GalA *p*α-(1→2)-Rha*p*) regions. In the latter, neutral sugar side chains, containing mainly L-arabinose, D-galactose and D-xylose, are covalently attached to the rhamnosyl residues of the backbone (Voragen, Pilnik, Thibault, Axelos, & Renard, 1995). Pectins are traditionally categorised as high methoxyl (HM) or low methoxyl (LM), with degrees of esterification (DE) of >50% and <50%, respectively (Rinaldo, 1996; Voragen et al., 1995). The degree of substitution of methyl esters determines the mechanism of formation of pectins gels. In HM pectins, gel formation occurs by the presence of relatively high concentrations of soluble solids, usually sucrose, and a low pH. On the other hand, LM pectins form gels by interaction with Ca^{+2} by the “egg box” mechanism (Rolin, 1993; Willats, Paul Knox, & Mikkelsen, 2006). Pectin is widely used as a gelling agent and stabilizer. It is commonly used in jams and jellies, fruit preparations, fruit drink concentrates, fruit juice, desserts and fermented dairy products (Tsoga, Richardson, & Morris, 2004). Although most plant tissues contain pectin, commercial production is based almost entirely on just a few sources that have the required properties (Thakur, Singh, & Handa, 1997). Currently, citrus peel and apple pomace are major sources of pectic substances around the world (Willats et al., 2006). In northern Mexico, apple is produced under climatically marginal conditions, especially in terms of winter chilling. This region provides more than half of the national apple production, the most important cultivar being ‘Golden Delicious’. An important portion of this production is considered to be low quality apple fruit, which is destined for industrial processing or is not picked up in local orchards due unprofitability of the low prices market. Apples remain in the orchard where they serve as animal feed or just become an infection focus as rodents and insects thrive.

The aim of this investigation was to extract pectin from low quality ‘Golden Delicious’ apple fruit and to determine its compositional and gelling capability.

2. Materials and methods

2.1. Materials

‘Golden Delicious’ apple fruit was kindly provided by a local orchard in northern Mexico. All chemical products were purchased from Sigma Chemical Co. (St. Louis, MO, USA).

2.2. Pectin extraction

Fresh apple was cut into four pieces and submitted to pectin extraction with 6% (w/v) citric acid at 100 °C for 30 min. The supernatant was filtered through a cheesecloth bag and cooled to 4 °C. The apple pectin was precipitated by ethanol-juice treatment 2:1 (v/v). The floating pectin was filtered through cheesecloth, rinsed with ethanol and then freeze-dried to obtain pectin powder.

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2.3. Monosaccharide composition

Monosaccharide composition was determined after pectin hydrolysis with 4 N trifluoroacetic acid at 120 °C for 4 h. The reaction was stopped on ice and the extract was evaporated under air at 40 °C, and rinsed twice with 200 μl of water. The evaporated extract was solubilised in 500 μl water. Inositol was used as internal standard. Samples were filtered through 0.45 μm (Whatman) and analysed by high performance liquid chromatography (HPLC) using a Supelcogel Pb column (300 × 7.8 mm; Supelco, Inc., Bellefont, PA) eluted with water (filtered 0.2 μm, Whatman) at 0.6 ml/min and 80 °C. A refractive index detector Star 9040 (Varian, St. Helens, Australia) was used. A Star Chromatography Workstation system control version 5.50 was used.

2.4. Proteins

Residual protein content in pectin powder was determined according to the Bradford method (Bradford, 1976).

2.5. Ash

Ash content was determined according to the AOAC methods (AOAC, 2002).

2.6. Degree of esterification (DE)

Pectin degree of esterification was determined as described by Rao, Van Buren, and Cooley (1993).

2.7. Intrinsic viscosity

Specific viscosity (η_{sp}) of pectin solution was measured with an AVS 400 capillary viscosimeter (Schott Geräte, Hofheim, Germany), equipped with an Oswald capillary tube (flow water time 75.15 s). The η_{sp} was related to the pectin concentration (η_{sp}/C) to obtain reduced viscosity η_{red} (ml/g) according to Rao et al. (1993). The intrinsic viscosity, $[\eta]$, was determined by the Mead, Kraemer and Fouss method (Kraemer, 1938; Mead & Fouss, 1942)*.

2.8. Pectin gels preparation

To form HM pectin gels, sucrose (60%) was added to the polysaccharide solution at 2% and 3% (w/v), pH was adjusted to 2.7 and the solutions were heated at 100 °C for 30 min (Rao et al., 1993). Gels were allowed to set overnight (12 h) at 4 °C.

2.9. Texture profile analysis

Texture profile analysis (TPA) of 2.0% and 3.0% (w/v) pectin gels, made in 6 ml glass flasks of 30 mm height and 25 mm internal diameter, was done with a TA.XT2i Texture Analyzer (RHEO Stable Micro Systems, Haslemere, England). The gels were deformed by compression at a constant speed of 1.0 mm/s to a distance of 3 mm from the gel surface using a cylindrical plunger (diameter 15 mm) (Carvajal-Millán, Guigliarelli, Belle, Rouau, & Micard, 2005). The parameters recorded include hardness, adhesiveness, springiness, cohesiveness, gumminess, chewiness and resilience. Gels were measured after set (12 h at 4 °C) and after a 48 h storage time at 4 °C.

2.10. Statistical analysis

Chemical determinations were done in triplicate and the coefficients of variation were lower than 5%. Texture measurements were done in triplicate and the coefficients of variation were lower than 10%. All results are expressed as mean values.

3. Results and discussion

3.1. Pectin extraction and characterisation

The yield of pectin extraction from apple fruit was 16% on a dry matter basis (w pectin/w apple fruit), which was similar to that reported by Marcon, Vriesmann, Wosiacki, and Beleski-Carneiro (2005) for pectins from apple pomace. The degree of esterification of the pectin extracted was estimated to be 57%, indicating that the polysaccharide was of the high-methoxyl type. By using a similar extraction method, Canteri-Schemin, Ramos-Fertonani, Wasczynskyj, and Wosiacki (2005) reported a 69% degree of esterification in pectin from mature apple pomace. The intrinsic viscosity ($[\eta]$) and viscosimetric molecular weight (Mw) of pectin gum were 307 ml/g and 112 kDa, respectively. Lower $[\eta]$ and Mw were reported by Constela and Lozano (2003) in HM apple pectin recovered by a similar acid extraction (Table 1). The pectin gum presented a galacturonic acid content of 65% (w/w). Residues of glucose, galactose, mannose, proteins and ash were also detected in this pectin gum (Table 2). This result indicated that the polysaccharide was mostly composed of galacturonic acid and a small quantity of neutral sugars, indicating that the polysaccharide was pectin. Accordingly, protein and ash contents, determined for this pectin gum, are similar to the values reported by Einhorn-Stoll, Kunzek, and Dongowski (2007) for apple pectin from other cultivars.

3.2. Pectin gelling capability

Pectin was solubized in 60% (w/v) fructose at pH 2.7; at concentrations of 2% and 3% (w/v). After heating, the solutions were kept at 4 °C during 12 h and then formed soft gels. HM pectin, unlike LM pectin, did not contain sufficient acid groups to gel with calcium ions. It has been suggested by Oakenfull (1991) that hydrogen bonding and hydrophobic interactions are important forces in the aggregation of HM pectin molecules. Actually, gel formation is caused by hydrogen bonding between free carboxyl groups on the pectin molecules, and the hydroxyl groups of neighbouring molecules. In a neutral or only slightly acid dispersion of pectin molecules, most of the unesterified carboxyl groups are present as partially ionised salts. Those that are ionised produce a negative

Table 1
Yield and physicochemical characteristics of ‘Golden Delicious’ pectin gum.

Yield%, (w pectin/w dry apple fruit)	16.0 ± 1.40
DE (%)	57.0 ± 1.90
$[\eta]$ (ml/g)	307 ± 2.60
Mw (kDa)	112 ± 3.20

All results are obtained from triplicates.

Table 2
Composition of pectin gum.

Galacturonic acid	65.0 ± 1.2
Arabinose	7.90 ± 1.1
Xylose	6.20 ± 1.60
Galactose	10.7 ± 1.20
Glucose	8.70 ± 0.01
Protein	0.80 ± 0.10
Ash	0.70 ± 0.10

Results are expressed in g/100 g pectin gum.
All results are obtained from triplicates.

Table 3
Effects of pectin concentration and time of storage on texture properties of gels.

Pectin (% w/v)	Hardness	Adhesiveness	Springiness	Cohesiveness	Gumminess	Chewiness	Resilience
After gel set							
2.0	10.2 b	39.4 b	0.88 a	0.43 a	8.9 a	1.7 a	0.04 a
3.0	20.4 a	44.6 a	0.85 a	0.42 a	8.6 a	1.4 a	0.05 a
After 48 h gel storage							
2.0	8.2 b	38.6 a	0.81 a	0.40 a	8.1 a	1.4 a	0.03 a
3.0	15.3 a	40.9 a	0.78 a	0.38 a	8.3 a	1.2 a	0.04 a

Mean values in the same column with different letters are significantly different ($P < 0.05$). All results are obtained from triplicates.

charge on the molecule which, together with the hydroxyl groups, causes it to attract layers of water. The repulsive forces between these groups, due to their negative charge, can be sufficiently strong to prevent the formation of a pectin network. When acid is added, the carboxyl ions are converted to mostly unionised carboxylic acid groups. This decrease in the number of negative charges, not only lowers the attraction between pectin and water molecules, but also lowers the repulsive forces between pectin molecules. Sugar further decreases hydration of the pectin by competing for water. These conditions decrease the ability of pectin to stay in a dispersed state. When cooled, the unstable dispersing of less hydrated pectin forms a gel, a continuous network of pectin holding the aqueous solution (Oakenfull, 1991). The rate at which gel formation takes place is also affected by the degree of esterification. A higher DE causes more rapid setting. Rapid set pectins (i.e. pectins with a DE of above 72%) also gel at lower soluble solids than do slow set pectins (i.e. pectin with a DE of 58–65%). Thus, HM pectin extracted from 'Golden Delicious' apple can be considered as a slow set pectin.

Table 3 shows the texture profile analysis of the pectin gels determined by TA-XT2i texturometer. The pectin gel hardness increased from 10.2 to 20.4 g on increasing the pectin concentration from 2% to 3% (w/v). The latter can be related to the polysaccharide chain aggregation phenomena, which are promoted as the polysaccharide concentration increases. The gels showed no significant ($p < 0.05$) difference of the other texture properties, except for adhesiveness. The pectin concentration significantly ($p < 0.05$) increased the adhesiveness of the gels. The adhesiveness had a positive effect on the thickness of the gels, and was an important factor governing the stability of the products during storage. The rheological stability of pectin gels at 2% and 3% (w/v) was determined after 48 h at 4 °C. After a period of storage, pectin gel hardness decreased from 10.2 to 8.2 and from 20.4 to 15.3 for the gels at 2 and 3% (w/v), respectively while no significant ($p < 0.05$) difference was found for the other texture properties. This rheological evolution could be due to an increase in pectin hydration as a result of a moderate acid hydrolysis of the pectin during storage. As a fact, HM pectin gels belong to the category of physically cross-linked gels whose three-dimensional structure is stabilized mainly by multiple hydrophobic interactions and hydrogen bonds in the junction zones of the polymeric network (Schmelter, Vreeker, & Klaffke, 2001).

4. Conclusions

Pectin with a high galacturonic acid content can be recovered from low quality apple fruit. Under the extraction conditions used in this study, the pectin recovered presented a high intrinsic viscosity and molecular weight, allowing the formation of a firm physical gel. The pectin concentration significantly ($p < 0.05$) increased the hardness and adhesiveness of the gels. Therefore, the pectin recovered could be used as food additive to texturize or stabilize different food products. Further research on its potential use as a food additive is needed. The results demonstrate that low quality apple fruit is a suitable raw material for industrial pectin extraction.

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