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Molecular structural differences between low methoxy pectins induced by pectin methyl esterase II: Effects on texture, release and perception of aroma in gels of similar modulus of elasticity

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ABSTRACT

Six low-methoxy pectins with different degrees of methylesterification and amidation, and molecular weights were used to prepare gels with similar moduli of elasticity by varying the concentrations of pectin and calcium phosphate. Five aroma compounds were added to the gels and their sensory textural properties, release and perception of aromas were investigated. Sensory firmness, springiness, adhesiveness, chewiness and cohesiveness differed according to the gel type, even though the moduli of elasticity were not significantly different ($p < 0.05$). Release and perception of aromas also displayed significant difference according to the gel type ($p < 0.05$). Low-methoxy amidated pectin exhibited the lowest release and perception for all the aroma compounds, while pectin-methylesterase-treated pectin gels exhibited relatively higher aroma release and perception. These results showed that the structural properties of pectins and gelling factors that increase the non-polar character of the gel matrices could decrease the release and perception of aromas in pectin gel systems.

1. Introduction

There has been considerable interest in better understanding the relationships between the perception of gel-type food texture and its structure in the production of gel-type food products. The replacement of ingredients in these foods, often leads to changes in food structure that are often perceived differently by consumers. Functional foods such as low-fat products and vegetarian products have not always been successful, leading to rejection by consumers, which is mainly due to the undesirable texture resulting from the replacement of ingredients (Renard, van de Velde, & Visschers, 2006). Aroma release is another important factor that determines the perception of aromas in gel-type food products. For example, the addition of hydrocolloids, which are common food additives with a wide variety of functional properties, often causes a reduced aroma perception; the mechanism underlying this change has yet to be fully explained (De Roos, 2000; Guichard, Issanchou, Descourvieres, & Etievant, 1991; Hansson, Giannouli, & van Ruth, 2003). Since foods generally contain low concentrations of aroma compounds, interaction of these compounds with other components in the food system can significantly affect the perception of aroma compounds. Since several studies revealed that the binding of aromas and hydrocolloids did not occur to a great extent in food products which contained large amounts of water (Boland, Buhr, Giannouli, & van Ruth, 2004; Boland, Delahunty, & van Ruth, 2006), the reduction in aroma perception of food products containing hydrocolloids requires an alternative explanation. Slower mass transfer caused by the increased viscosity of products containing hydrocolloids could explain the decreased aroma release and perception by consumers (Taylor, Besnard, Puaud, & Linforth, 2001). The effects of hydrocolloids and texture on the perceived aroma intensity, known as cross-modal interactions, have been investigated. Taylor et al. (2001) indicated that the rate of aroma release was correlated with the observed change in sensory perception among gel samples, and that the perception of diacetyl and ethyl butyrate was directly influenced by the hardness of the gels. They reported a less intense perception of aroma in gels with higher hardness, despite similar concentrations of the aroma being released into the nose. Related to the strength of the gels and the release of aroma compounds, it was reported that the increase of gel strength by high pectin concentration retained more hydrophobic compounds compared to hydrophilic ones, due to the dense network of increased non-polar pectin micelles (Boland et al., 2006; Hansson, Giannouli et al., 2003; Hansson, Leufvén, & van Ruth, 2003). Moreover, reduced perception of aroma and sweetness were reported as perceived thickness increased, (Boland et al., 2006; Guichard et al., 1991). We observed similar results in our previous research on the relationship between molecular structure of pectin, perception and release of aroma compounds in gels of pectins

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with known molecular structural properties (Kim, Kim, Yoo, & Kim, 2010). The influence of gel strength on the perceived aroma intensities was much greater than that of aroma release; accordingly, decreased perception of aroma in pectin methylesterase-treated gels with higher strength was observed. Since, the gels were made of the same ingredients, the observed decrease in perception was solely induced from the strength of the gel not from the difference of pectin concentration, which was distinct from other studies. Even though the effects of structural characteristics of the pectins on the texture and aroma release from the gels could be clearly examined from the previous study, it is still uncertain that the decreased perception of aroma was either due to the difference of structure of pectins or due to the increased gel strength. The relationship between the release and perception of aroma in the pectin gel systems also remains unclear.

From the view of industrial application, each food product has desired gel strength and the desired strength could be obtained from pectins with diverse molecular structure as demonstrated by our previous study (Kim et al., 2008). We postulated that if the gel strength could be consistent between gels, the effects of strength of the gels on the release and on the perceived aroma intensities could be countervailed. In addition, the effects of structural differences on the release and perception of aroma could be elucidated.

This study was conducted to characterise the effects of the structural properties of pectins on the release and perception of aroma in pectin gels of similar strength, and to elucidate the relationships between molecular structural properties of pectin, aroma release and perception in pectin gels.

2. Materials and methods

2.1. Materials

A low-methoxy pectin, LM-13CG, and a low-methoxy amidated pectin, LM-101AS, were used (CP Kelco, Atlanta, GA) in this study. Four types of modified pectins were produced (two from high-methoxy pectin (YM-100H, CP Kelco, Atlanta, GA), one from low-methoxy pectin and one from low-methoxy amidated pectin) *via* the reaction of a salt-independent pectin methylesterase isozyme from Valencia orange peel (P5400, Sigma Chemical Co., St. Louis, MO). The treated pectins were designed to have different molecular weights, degrees of methylesterification and degrees of amidation. The detailed descriptions of the demethylesterification and the molecular properties of pectins have been reported in the previous study (Kim et al., 2008). The molecular structural properties of the pectins are given in Table 1. All edible grade aromas and other chemicals were analytical grade reagents from Sigma–Aldrich. Five volatile compounds with different hydrophobicities and functional groups were used to measure release of aroma compounds from pectin gels. Benzaldehyde, citral, diacetyl, isoamyl acetate and menthol, all of edible grade, were purchased from Sigma–Aldrich; their physicochemical properties are presented in Table 2.

Table 2
Physicochemical properties and structures of volatile compounds.

Aroma compound	Formula	Boiling point (°C) [a]	Molecular weight	Log *P* [b]
Benzaldehyde	C_7H_6O	179	106.12	1.48
Citral	$C_{10}H_{16}O$	229	152.24	3.45
Diacetyl	$C_4H_6O_2$	87–88	86.09	−1.34
Isoamyl acetate	$C_7H_{14}O_2$	142	130.19	2.25
Menthol	$C_{10}H_{20}O$	212	156.27	3.40

[a] Obtained from the Merck Index.
[b] Hydrophobicity, http://www.syrres.com/esc/physdemo.htm.

2.2. Gel preparation and characterisation by Young's modulus

Pectin was dissolved in deionised water with magnetic stirring for 24 h. Sucrose was dissolved and calcium phosphate was dispersed evenly with stirring then gluconolactone was added to the solution and dissolved completely. Since gluconolactone slowly releases hydrogen ion, resulting in a slow decrease in pH, gels could be prepared uniformly by using it. Final composition of the pectin gel is presented in Table 1. Different amounts of pectin and calcium phosphate had to be applied so that there were no significant differences in their moduli of elasticity ($p < 0.05$), due to the large differences in calcium sensitivity of pectins induced by their molecular weight, degree of methylester and acid amide (Table 1). Gel strength was characterised during compression at large degree of deformations using a TA.XT 2i texture analyser. To determine the amount of pectin and calcium phosphate of each gel, 15-g gel mixtures were transferred into 15-mm diameter cylindrical tubes, sealed and refrigerated for 24 h. The gels were equilibrated at room temperature (25 °C) before the compression measurement and cut with two parallel razor blades into four pieces of 1.5 cm height. Compression measurements were determined using a TA.XT 2i texture analyser probe at a constant speed of 1 mm/s, until compression was 35% of the initial height of the samples (Boland et al., 2006). Young's modulus (modulus of elasticity, *E*) was calculated from the three replicates of force deformation data. True stress and true strain were calculated according to the method described by Konstance (1993). True stress–strain curve was derived and the slope of the true stress–strain curve provides the value of modulus of elasticity (Dobraszczyk & Vin-

Table 1
Pectin molecular properties, pectin gel composition, pH and Young's moduli.

	L40	H41	LA39	L6	H6	LA18
Molecular properties of pectins[a]						
Peak molecular weight ($\times 10^5$)	1.6	3.8	2.1	1.8	3.7	2.0
Degree of methylesterification (%)	39.9	40.9	39.0	6.5	6.3	18.0
Degree of amidation (%)	0	0	14	0	0	14
Gel composition and properties						
Pectin (%w/v)	1.00	0.47	1.00	0.67	0.25	0.33
Calcium phosphate (%w/v)	0.10	0.05	0.10	0.05	0.05	0.05
Sucrose (%w/v)	15	15	15	15	15	15
pH[b]	3.23	3.23	3.23	3.23	3.23	3.23
Young's modulus [c](N/m^2)	56.89	56.86	56.75	56.44	56.91	57.08

[a] All values were measured in previous study (Kim et al., 2008): Means of triplicates.
[b] 0.45–0.47% gluconolactone was used to adjust pH.
[c] Means of triplicates. Not significantly different at $p < 0.05$.