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Effects of Calcium Chloride and Alum on Firmness Retention of Scallion Pickles

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Summary

The effects of $CaCl_2$ and alum on firmness retention of scallion pickles were examined. The pickles (control) softened rapidly during pickling, but the pickles with $CaCl_2$ or alum retained their firmness during 6 months of storage, and after 1 year, their firmness decreased. However, pickles with $CaCl_2$ and alum were firmer than control. The amount of galacturonic acid in control decreased considerably during storage, but that of galacturonic acid in pickles with $CaCl_2$ and alum did not decrease during 6 months of storage, and decreased gradually after 1 year. The amount of galacturonic acid remaining in the scallions was as follows: pickles with $CaCl_2$ > pickles with alum > control. There was a significant correlation between the firmness of pickles and the solubilization of pectic substances from cell walls. During storage, the degree of esterification (DE) of pectic substances in pickles decreased. Decrease of DE of pectin shifted the calcium binding ability. $CaCl_2$ and alum affected pectin insolubility inside the cell walls and middle lamella and hence intercellular cohesion.

Introduction

Calcium chloride is now commonly used in brines during cucumber fermentation and pickle storage.[1] Its presence has been shown to protect against enzymatic and possible nonenzymatic softening.[2~6] Ca^{2+} bonding to galacturonans is influenced by several factors such as the degree of esterification (DE), ionic strength and pH.[7] Although cations are believed important for maintaining structural integrity, the effect of cations on the texture of scallion pickles have not been examined.

The objective of this study was to determine the effects of $CaCl_2$ and alum on firmness retention of scallion pickles. In addition, the relationship between pectic changes and the softening of scallion pickles during storage was determined.

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Material and methods

1) Sample preparation. Bulbs from scallions *(Allium Bakeri REGEL)* harvested in Tottori were used. The skins of the scallion bulbs were peeled off and tops and roots were cut off.

2) Processing. Fresh scallion (1.0 kg) were placed into a vinegar-brine (80 g NaCl, 400 ml vinegar and 400 ml water) in a 2000 ml glass jar, and stored for 2 weeks at room temperature.

A sugar-vinegar solution (150 g sugar and 400 ml vinegar) was heated until the sugar melted, and then cooled, and used for pickling. 1% calcium chloride or 1% burnt alum were added to a sugar-vinegar solution. 20 g of scallions pre-acid-brined for 2 weeks were placed into a 30 ml of sugar-vinegar solution, a 30 ml of sugar-vinegar solution with $CaCl_2$ or a 30 ml of that with alum in 60 ml glass jars. These were designated as pickles (control), pickles with $CaCl_2$ and pickles with alum, respectively. These pickles were stored at room temperature for 2 years.

3) Firmness measurement. After 6 months, 1 year, and 2 years, firmness of the pickles was measured by a Kiya hardness tester (Kiya Seisakusho Ltd., Tokyo), and the unit of hardness was indicated as kg. The experimental results are the average of ten measurements. In addition, firmness of pickles of 1 year and 2 years of storage was measured by Curdmeter (Iio Electric Co., M-301 A, Tokyo) and expressed as breaking strength.

4) Extraction of pectic substances.

This was performed by the same method reported previously.[8~10] The pectic substances were fractionated by successive extraction using three reagents from raw or pickled scallions. The extracts with 0.01N HCl solution (pH 2.0), 0.1M sodium acetate buffer solution (pH 4.0), and 2% sodium hexametaphosphate solution (pH 4.0) were designated as pectin A (PA), pectin B (PB), and pectin C (PC), respectively.

5) Fractionation of pectic substances by DEAE-cellulose column chromatography and gel filtration. This was performed by the same method reported previously.[9~10]

Results and discussion

1. Effects of $CaCl_2$ and alum on firmness retention of scallion pickles

The changes in the firmness of scallion pickles and the pH of pickle (sugar-vinegar) during storage are shown in Fig. 1 (hardness) and Fig. 2 (breaking strength). The scallions retained their firmness after 2 weeks of acid-brining, but pickles (control) softened rapidly during pickling. The firmness of pickles with $CaCl_2$ increased during 6 months of storage, and then decreased gradually. Addition of $CaCl_2$ resulted in greater initial firmness and greater retention of firmness for pickles during the 6-month storage period. The pickles with alum also retained their firmness during 6 months of storage, but after 1 year, the firmness decreased. However, pickles with $CaCl_2$ and alum were firmer than control.

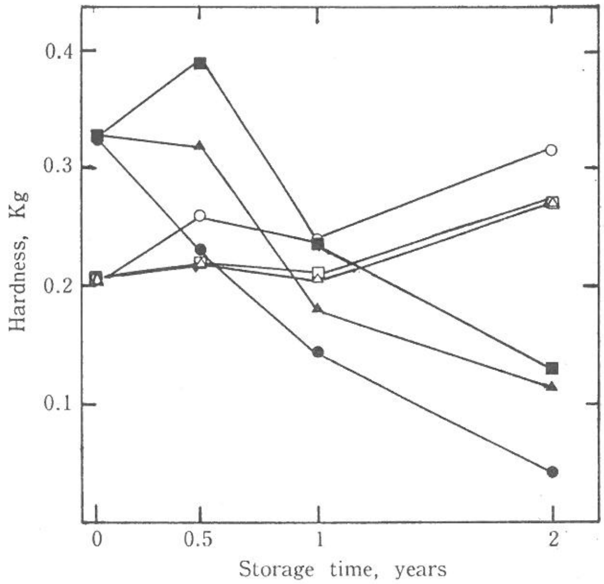

Fig. 1. Changes in firmness of scallion pickles and the pH of sugar-vinegar solution during storage

The pH level of a sugar-vineger solution increased during storage. However, the pH level of sugar-vinegar with $CaCl_2$ and alum were same as the initial pH level during 1 year, and then increased.

2. Change in pectic composition of scallion pickles

The change in pectic composition of pickles during storage is shown in Fig. 2. The amount of galacturonic acid in pickles (control) decreased considerably during storage. However, the amount of galacturonic acid in pickles with $CaCl_2$ and alum did not decrease during 6 months of storage, and decreased gradually after 1 year. The amount of galacturonic acid remaining in the scallions was as follows: pickles with $CaCl_2$ > pickles with alum > control. There was a significant correlation between the firmness of pickles and the solubilization of pectic substances from cell walls (Fig. 3). $CaCl_2$ and alum affected pectin insolubility inside the cell walls and middle lamella.

3. Change in the degree of esterification of pectic substances in scallion pickles during storage

The change in the DE of pectic substances in scallion pickles during storages is shown in Table 1. During storage, the DE of PA, PB and PC in scallions decreased. The activity of pectin methylesterase (PME) in scallion pickles continued to be considerably active even after 1 month of storage.[11] PME affected the demethoxylation of pectic substances in scallion pickles during storage.[11] It was known already that low esterified pectin forms water-

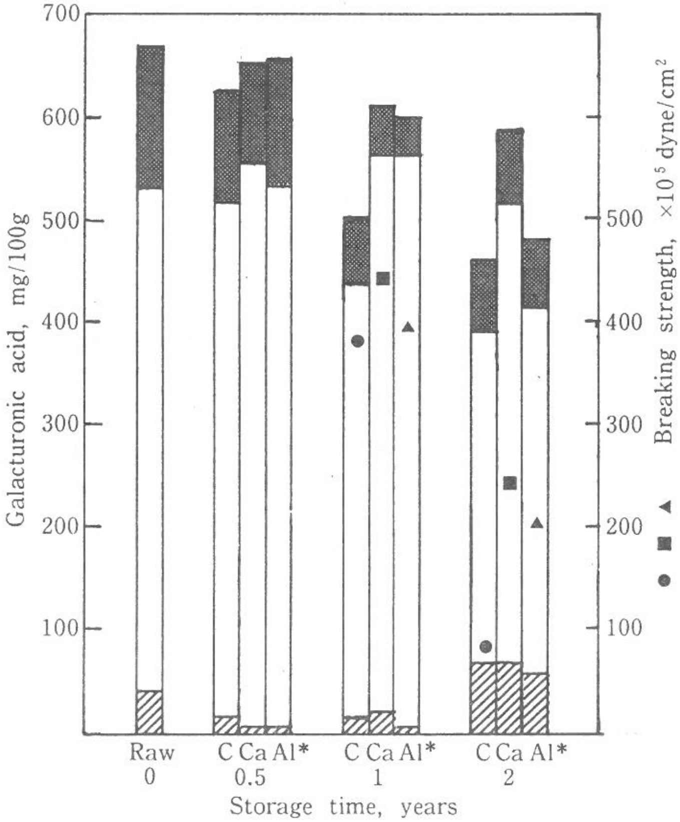

Fig. 2. Changes in the amount of galacturonic acid and breaking strength of scallion pickles during storage

* C: pickles (control), Ca: pickles with $CaCl_2$, Al: pickles with alum

PA: Extraction with 0.01N HCl (pH 2.0) at 35°C.

PB: Residues of PA were extracted with 0.1M sodium acetate buffer solution (pH 4.0) at 35°C.

PC: Residues of PB were extracted with 2% sodium hexametaphosphate solution (pH 4.0) at 90°C.

● Breaking strength of pickles (control)

■ Breaking strength of pickles with $CaCl_2$

▲ Breaking strength of pickles with alum

insoluble calcium precipitates.[7] Decrease of DE of pectin shifted the calcium binding ability. Cations affected solubilization of pectin and hence intercellular cohesion. The DE of pectin decreased and migration of calcium ion led to firming of cell wall and middle lamella pectin gel.

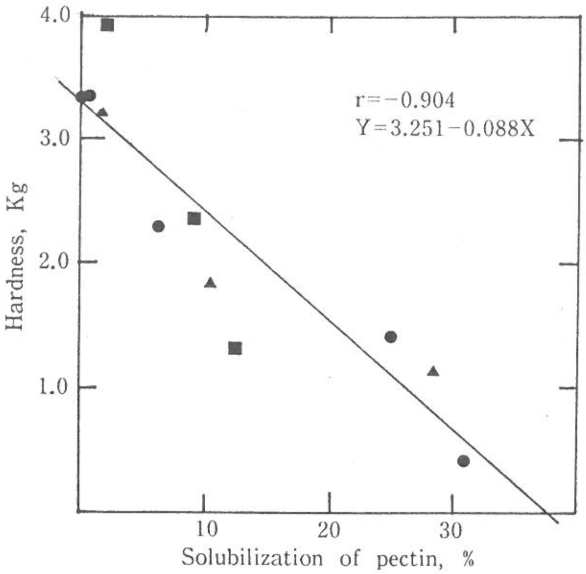

Fig. 3. The correlation between hardness of scallion pickles and the solubilization of pectic substances from cell walls

● ■ ▲ : see Fig. 1.

Table 1. Change in the degree of esterification of pectic substances in scallion pickles during storage, %

Sample	Storage time	Pickles (control)			Pickles with $CaCl_2$			Pickles with alum		
		PA*	PB*	PC*	PA	PB	PC	PA	PB	PC
Raw scallions		48.2	24.4	32.4						
Pre-brined scallions	2 weeks	42.8	17.6	18.6						
Pickles	6 months	40.0	9.2	15.2	38.2	8.0	9.9	17.2	7.1	6.6
Pickles	1 year	17.8	13.0	7.9	13.3	11.6	12.2	20.3	5.9	7.9
Pickles	2 years	10.2	6.1	8.0	17.3	15.0	15.5	15.4	9.1	11.1

* PA, PB and PC: see Fig. 2.

4. Change in DEAE-cellose column chromatograms of pectic substances in scallion pickles during storage

The DEAE-cellulose column chromatograms of PA, PB and PC in raw scallions and pickles after 2 years of storage are shown in Fig. 4, Fig. 5, and Fig. 6, respectively. The fractions I, II and III were neutral polysaccharides, weakly acidic polysaccharides (pectin) and pectic acid, respectively.[12]

The chromatograms changed during storage, especially in control. The galacturonic acid of PA in control was eluted later in fraction II than it was in the raw scallions and pickles with $CaCl_2$ and alum. This suggested that PA in the former (control) was more demethoxylated than PA in the latter, since the low methoxyl pectin usually eluted in fraction III and later in fraction Ⅱ.

A great change in elution patterns in PB was not found during storage. Almost of all galacturonic acid of PC in pickles with $CaCl_2$ and alum was eluted in fraction Ⅲ. Elution patterns were similar to that of raw scallions. However, the PC in control was eluted more in fraction Ⅱ than fraction Ⅲ. It seemed that pectic substances were depolymerized.

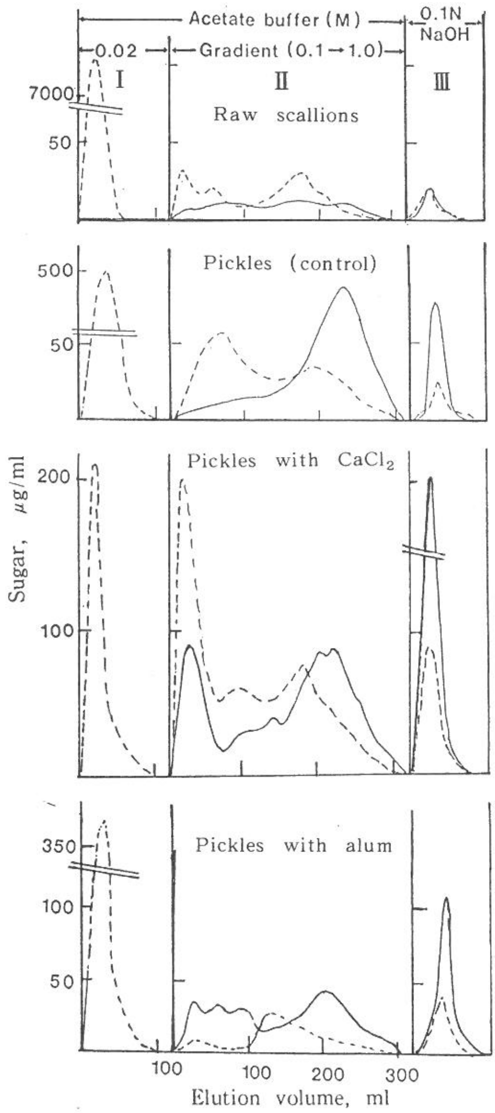

Fig. 4. Change in DEAE-cellulose column chromatogram of PA in scallion pickles after 2 years of storage

— galacturonic acid, ⋯ neutral sugar.

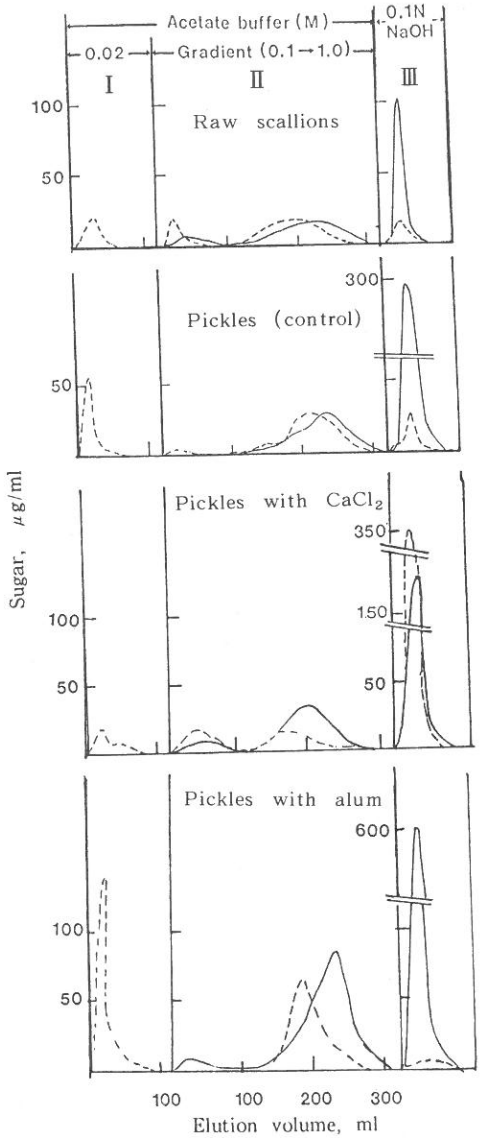

Fig. 5. Change in DEAE-cellulose column chromatogram of PB in scallion pickles after 2 years of storage

— galacturonic acid, ··· neutral sugar.

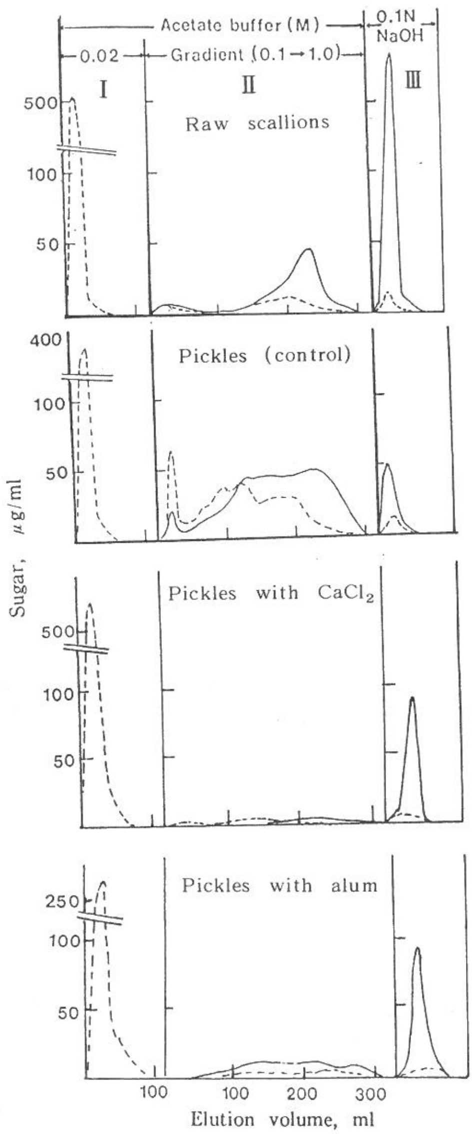

Fig. 6. Change in DEAE-celluose column chromatogram of PC in scallion pickles after 2 years of storage

— galacturonic acid, ··· neutral sugar.

5. Change in gel filtration profiles of pectic substances during storage

The gel filtration profiles of fraction II and III of PA, PB and PC in raw scallions and pickles after 2 years of storage separated by DEAE-cellulose column chromatography are shown in Fig. 7. The pectic substances of fraction II of PA in raw scallions were of comparatively high molecular weight (MW; $>5\times10^5$). After 2 years of storage, MW of PA eluted in fraction Ⅱ decreased, especially the MW of contorol. The MW of PB-fraction Ⅱ did not change, but MW of PB-fraction Ⅲ of contorol and pickles with alum decreased after 2 years of storage. The MW of PC in contorol and pickles with alum decreased. This shows that MW of the pectic substances in contorol decreased greatly, and that in pickles with $CaCl_2$ did not change greatly. Excessive softening was observed in contorol especially after 2 years of storage. It seemed that the pectic substances demethoxylated by pectin methylesterase was degraded by polygalacturonase, and then released into sugar-vinegar-brine during storage. However, $CaCl_2$ and alum affected pectin insolubility inside the cell walls and middle lamella and hence intercellular cohesion.

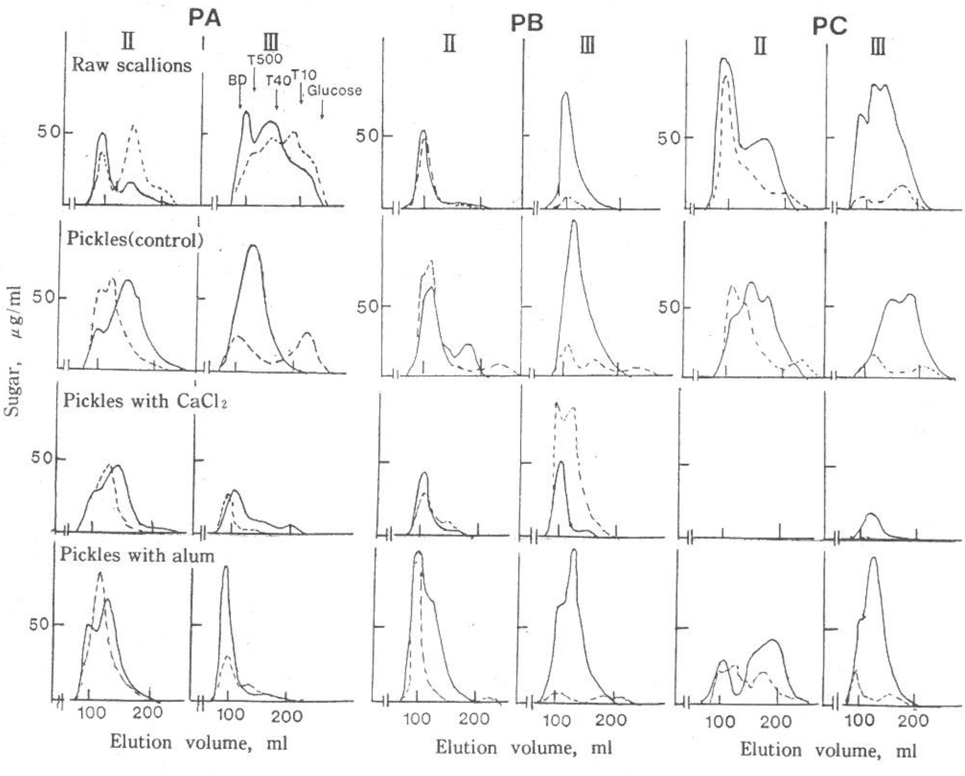

Fig. 7. Change in the gel-filtration profiles of pectic substances in scallion pickles by Sepharose CL 6B after 2 years of storage

— galacturonic acid, ··· neutral sugar.
BD, T500, T40, T10: Blue dextran, Dextran T500, Dextran T40, Dextran T10.

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