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Pectic Changes in Pre-brined Scallion Pickles During Storage

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Summary

The relationship between softening of pre-brined scallion pickles and pectic changes during storage for 2 years was investigated. The pickles softened gradually during storage. The pectic substances were extracted successively with 0.01N HCl (pH 2.0), 0.1M acetate buffer (pH4.0) and sodium hexametaphosphate solution (pH 4.0). The extracts were designated as PA, PB and PC, respectively. After acid-brining for 2 weeks, PA decreased. After 1 year of storage, galacturonic acid in scallion pickles decreased rapidly. During acid brining and pickling, the degree of esterification (DE) of PA, PB and PC in scallion pickles also decreased. During storage, the DEAE-cellulose column chromatograms of PA and PC in scallion pickles changed, but the neutral sugar composition of pectic substances did not change greatly.

Introduction

Scallion pickles are traditional and typical of Japan. Changes in ascorbic acid, sensory quality and reduction of sugar during storage were investigated previously.[1~3] However, research data showing a relationship between pectic changes and the softening of scallion pickles, except cucumber pickles,[4~8] was not found.

Firmness is an important characteristic of pickles, and so excessive softening is a common problem. The relationship between pectic changes and softening of scallion pickles during storage for 2 years was investigated.[9] There was a correlation between the firmness of pickles and the solubilization of pectic substances taken from the cell walls of these pickles.[9]

The objective of this investigation was to evaluate the relationship between pectic changes and the softening of scallion pickles during storage, and to focus on DEAE-cellulose column chromatogram.

Material and methods

1) Sample preparation. Bulbs of 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 scallions (1.0 kg) were placed into a vinegar–brine (80 g NaCl, 400 ml vinegar and 400 ml water) in a 2,000 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 it was cooled, and used for pickling. The acidity of vinegar was 4.3%. 20g of scallions pre–acid–brined for 2 weeks were placed into a 30 ml of sugar–vinegar solution in 60 ml glass jars. The twelve jars were prepared for this experiment. These pickles were stored at room temperature for 2 years.

3) Firmness measurement. After 6 months, 1 year, and 2 years, respectively, firmness of the pickles was measured by a Kiya Hardness Tester (Kiya Seisakusho Ltd., Tokyo). The experimental results are the average of ten measurements.

4) Extraction of pectic substances. [10~13] The pectic substances were fractionated by successive extraction using three reagents from raw or pickled scallions. Pectic substances in samples homogenized with 0.01N HCl solution (pH 2.0) were extracted with the same solution at 35°C, 5 times every 24 hr. The extracts were designated as pectin A (PA). Subsequently, the residues of PA were extracted with a 0.1M sodium acetate buffer solution (pH 4.0) at 35°C, 8 times every 24 hr. These extracts were designated as pectin B (PB). The pectic substances in the residues of PB were extracted with a 2% sodium hexametaphosphate solution of pH 4.0 at 90°C, 4 times every 3.5 hr. These extracts were designated as pectin C (PC). Each extract was concentrated to about 10 ml at pH 4.0 and dialyzed against distilled water (2l) at 5°C 2 times every 24 hr. The amount of total sugar was determined by the phenol sulfuric acid method. [14] The neutral sugar fraction was separated from PA and PC by DEAE–cellulose column chromatography. [12)13)] The amount of galacturonic acid in a acidic sugar fraction was determined by the carbazole method. [15] The degree of esterification (DE) of PA, PB and PC was determined by a gas chromatographic method. [16] Neutral sugar composition was measured by a gas chromatographic procedure. [17]

5) Fractionation of pectic substances by DEAE–cellulose column chromatography. This was performed by the same method reported previously. [12)13)]

Results and discussion

1. Change in firmness of scallion pickles during storage

Changes in the firmness of scallion pickles and the pH of pickle (sugar–vinegar) during storage are shown in Fig. 1. The scallions retained their firmness after 2 weeks of acid–brining, but pre–acid brined pickles softened gradually during pickling. The pH level of the pickle increased during storage.

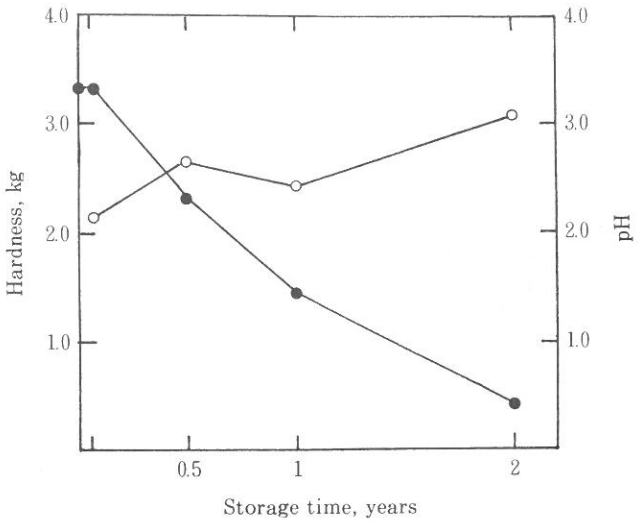

Fig. 1. Changes in firmness of pre-brined scallion pickles and the pH of sugar-vinegar solution during storage.

● Hardness, ○ pH

2. Change in pectic composition of scallion pickles

The change in pectic composition of pre-brined scallion pickles during storage is shown in Fig. 2. The amount of galacturonic acid of PA, PB and PC in raw scallions 100 g was 40.9 mg, 492.1 mg and 137.0 mg, respectively. The pectic composition was PB > PC > PA. After acid-brining for 2 weeks, the PA decreased, and PB increased. This converse tendency continued during 6 months of pickling. After 1 year of storage, galacturonic acid in scallion pickles decreased rapidly and PB also decreased. After 2 years of storage, PA increased. PA seemed to have increased because it was more easily extracted by the depolymerization. There was a significant correlation ($r = -0.956$, $p < 0.01$) between the firmness of pickles and the solubilization of pectic substances from cell walls.[9] This suggested that the cause of softening of scallion pickles was the solubilization of pectic substances from cell walls.

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

Change in the DE of pectic substances in scallion pickles during storages is shown in Fig. 3. The DE of PA, PB and PC in raw scallions was 48.1%, 24.4% and 32.4%, respectively. The DE of pectic substances in raw scallions was comparatively low. During acid-brining and pickling, the DE of PA, PB and PC in scallions decreased.

The relationship between pectin methylation and tissue firmness was examined in cucumber pickles exposed to pre-brining and brining treatments.[6] The firmness declined when the DE was reduced below the critical level of 12.3 ± 1.2.[6] Excessive demethoxylation is believed to change the configuration of pectin macromolecules which contributes to the loosening of middle lamella-cell wall components and to softening.[6] The DE of pectic substances in pre-

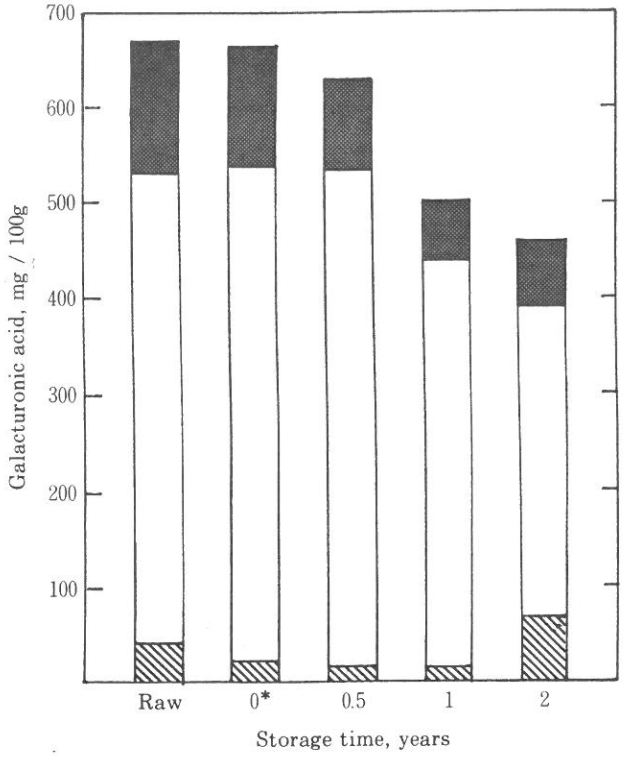

Fig. 2. Change in the amount of galacturonic acid in pre-brined scallion pickles during storage.

▨ 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.
*Scallion acid-brined for 2 weeks.

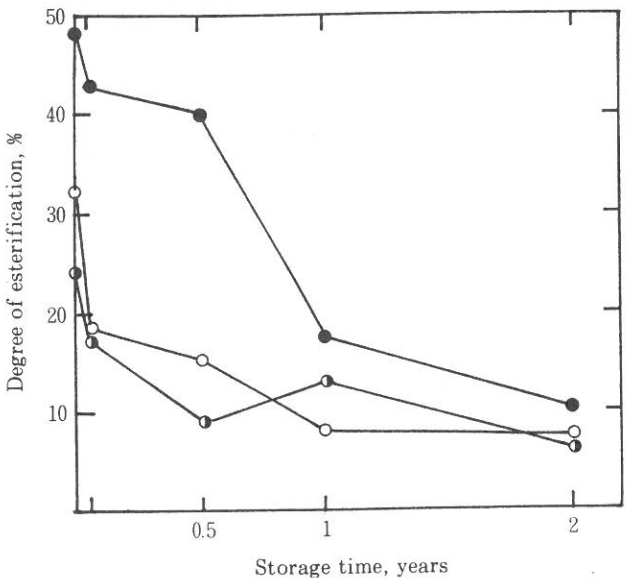

Fig. 3. Change in the degree of esterification of pectic substances in pre-brined scallion pickles during storage.

● PA, ◑ PB and ○ PC: See Fig. 2.

brined pickles after 2 years of storage was below 12.3%. These results suggested that the firmness was related to the DE of pectins when the DE was less than 12.3.

4. Change in DEAE-cellulose column chromatograms of pectic substances in pre-brined scallion pickles during storage

The change in DEAE-cellulose column chromatograms of PA, PB and PC in pre-brined scallion pickles during storage is 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)13)18)]

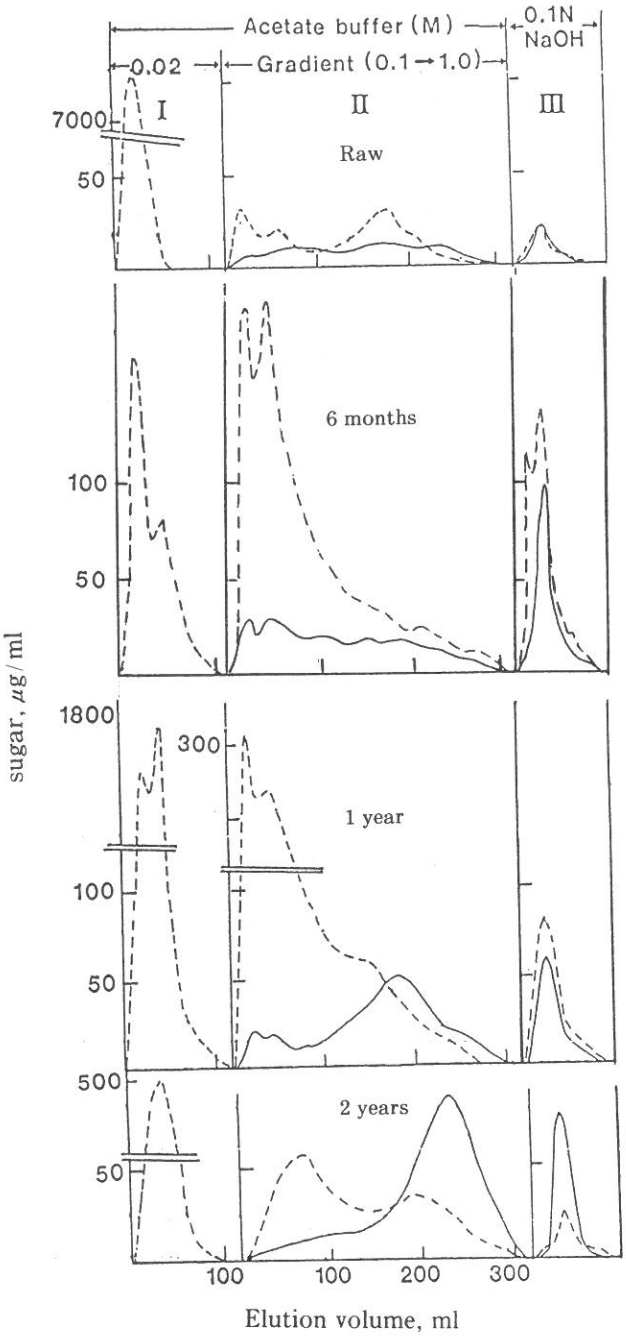

Fig. 4. Change in DEAE-cellulose column chromatogram of PA* in pre-brined scallion pickles during storage.

– galacturonic acid, ··· neutral sugar.

* See Fig. 2.

The PA of raw scallions was eluted more slowly in fraction II than the PA of asparaguses (a monocot yledonous plant)[19] and Japanese radish roots (a dicot yledonous plant).[17)19)] This suggested that the DE of PA in scallions was lower than the DE of asparaguses and Japanese radish roots. The amount of PA eluted in fraction III was small.

The galacturonic acid of PA in pre-brined pickles was eluted gradually later in fraction II than it was in the raw scallions. This suggested that the PA in pre-brined pickles was demethoxylated during storage.

The PB peak was detected at about 230 ml in fraction II of raw and pickled scallions (Fig. 5). Since the low methoxyl pectin was usually eluted later in fraction II,[18] DE of PB was lower than DE of PA. The PB peak in fraction III was higher than the PA peak in fraction III. This also suggested that the DE of PB was lower than the DE of PA, although a great change

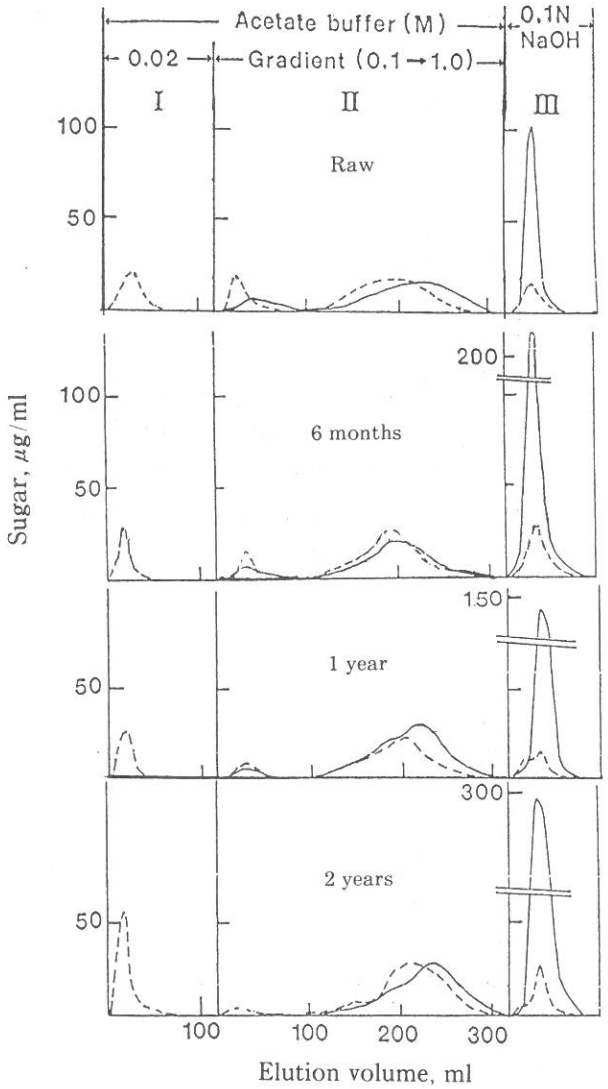

Fig. 5. Change in DEAE-cellulose column chromatogram of PB* in pre-brined scallion pickles during storage.

— galacturonic acid, ··· neutral sugar.

* See Fig. 2.

in elution patterns in fraction II of PB was not found during storage.

The galacturonic acid elution pattern of PC in raw scallions was similar to that of PB (Fig. 6). The PC in pre-brined pickles was eluted more in fraction II than in fraction III. It seemed that pectic substances were depolymerized by enzymatic (pectin methylesterase and polygalacturonase) or non-enzymatic degradation.

The neutral sugar eluted in fraction I is not pectin. The amount of neutral sugar eluted in fraction I from raw scallions and pre-brined pickles was as follows: PA > PC > PB, respectively.

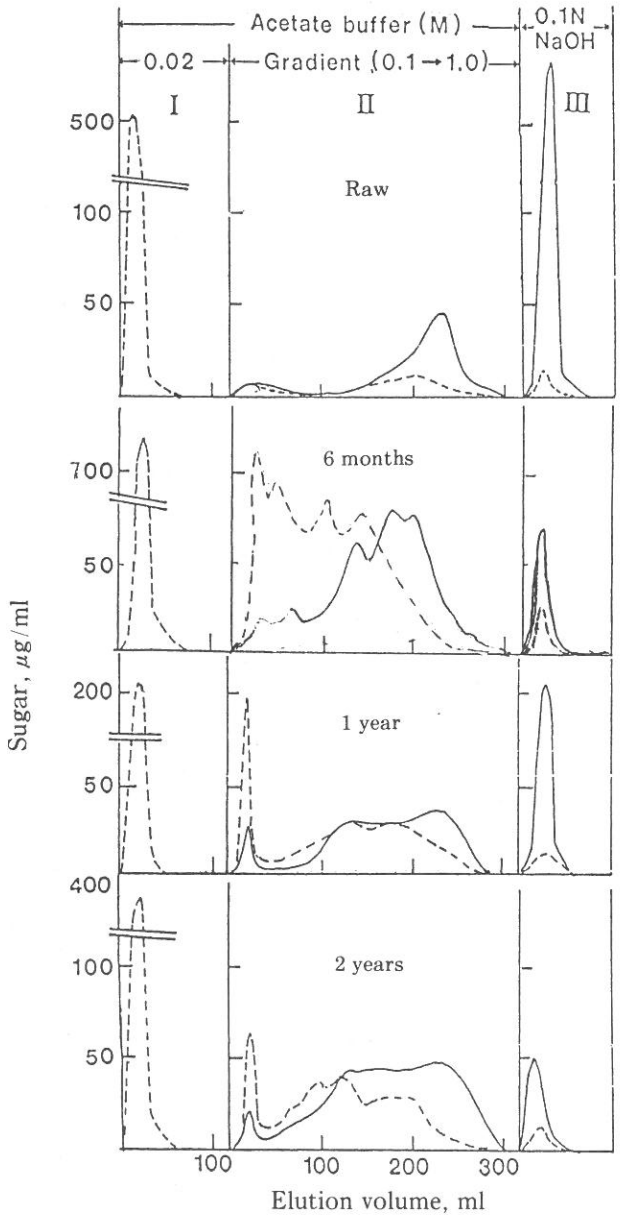

Fig. 6. Change in DEAE-cellulose column chromatogram of PC* in pre-brined scallion pickles during storage.

— galacturonic acid, ··· neutral sugar.

* See Fig. 2.

5. Change in the composition of monosaccharides in pectic substances of pre-brined scallion pickles during storage

Change in the composition of monosaccharides in neutral and acidic sugars (pectic substances) of raw scallion and pre-brined pickles after 1 year and 2 years of storage is shown in Table 1 ~ Table 3. The main neutral sugar in pectic substances was galactose. The neutral sugar composition of pectic substances in scallion bulbs rather resembled that of monocotyledonous plants such as onions,[20] garlic bulbs,[21] and East Indian lotus rhizomes[13] than that of *Gramineae* such as bamboo shoots.[19)22)] The neutral sugar composition did not change greatly during storage.

Table 1. The composition of monosaccharides in neutral and acidic sugars of raw scallions separated by DEAE-cellulose column chromatography

Type of pectin	Fraction* by DEAE	Percentage of II III	Neutral** sugar %	Composition of monosaccharides, %					
				Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose (Fructose)
PA	I		100	0.6	0.2	0.2	46.1	trace	52.9
	II	79.0	61.2	2.2	18.3	3.6	3.5	51.8	20.6
	III	21.0	50.2	2.7	9.1	5.9	7.8	70.6	3.8
PB	I		100	0	trace	10.8	36.8	52.4	0
	II	45.2	51.4	4.5	9.8	6.4	3.4	75.9	0
	III	54.8	13.4	3.9	5.1	3.2	3.0	84.8	0
PC	I		100	1.9	6.3	3.0	3.5	81.8	3.3
	II	51.6	24.5	trace	11.5	7.5	7.8	73.1	0
	III	48.4	9.3	1.5	10.5	17.0	7.8	63.4	trace

* Fraction obtained by DEAE-cellulose column chromatography (See Fig. 4~6).
** Neutral sugar (%) = neutral sugar ÷ pectic substances (galacturonic acid + neutral sugar) × 100.

Table 2. The composition of monosaccharides in neutral and acidic sugars of scallion pickles after 1 year of storage separated by DEAE-cellulose column chromatography

Type of pectin	Fraction by DEAE	Percentage of II III	Neutral sugar %	Composition of monosaccharide, %					
				Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose
PA	I		100	0	11.7	3.9	4.0	72.8	7.6
	II	79.4	79.4	6.0	23.3	3.0	1.6	66.1	0
	III	20.6	62.8	2.5	6.8	10.2	9.8	50.1	20.8
PB	I		100	4.2	3.8	3.8	1.9	86.3	0
	II	51.5	33.8	1.8	2.2	2.9	1.2	92.0	0
	III	48.5	10.3	0.3	1.7	20.1	3.7	74.1	0
PC	I		100	2.9	10.2	7.7	7.8	70.7	0.9
	II	76.5	51.7	10.5	4.8	7.2	2.4	75.1	0
	III	23.5	17.7	5.7	3.1	12.8	7.0	51.1	20.4

Table 3. The composition of monosaccharides in neutral and acidic sugars of scallion pickles after 2 years of storage separated by DEAE-cellulose column chromatography

Type of pectin	Fraction by DEAE	Percentage of II III	Neutral sugar %	Composition of monosaccharide, %					
				Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose
PA	I		100	0.4	43.2	0.4	1.3	54.6	trace
	II	87.7	47.4	3.6	46.5	4.4	0.8	44.7	0
	III	13.6	30.8	0.4	47.4	2.4	17.6	8.9	23.4
PB	I		100	14.1	21.2	5.7	3.2	55.8	0
	II	35.3	49.8	2.4	18.2	10.6	0	68.8	0
	III	64.7	6.6	3.6	11.3	16.1	0	69.1	0
PC	I		100	1.5	3.2	1.1	1.7	92.6	trace
	II	88.4	49.1	2.4	5.2	6.9	0.6	85.0	0
	III	11.6	20.7	2.6	8.5	13.7	5.2	54.8	15.1

References

1) Nakamura, M. and Shimada, Y.: *Toyoko Gakuen Jyoshi Tandai Kiyo*, **11**, 17 (1973)
2) Shimada, Y. and Katayama, M.: *Toyoko Gakuen Jyoshi Tandai Kiyo*, **12**, 15 (1974)
3) Okuda, S., Kotani, I., Inoue, Y., Okawara, E., Miyanaka, A., and Katsuki, F.: *Nippon Eiyo Shokuryo Gakkaishi (J. Jpn. Soc. Nutri. Food Sci.)*, **42**, 326 (1989)
4) Sinstrunk, W. A. and Kozup, J.: *J. Food Sci.*, **47**, 949 (1982)
5) McFeeters, R. F., Fleming, H. P., and Thompson, R. L.: *J. Food Sci.*, **50**, 201 (1985)
6) Hudson, J. M. and Buecher, R. W.: *J. Food Sci.*, **51**, 138 (1986)
7) McFeeters, R. F., Senter, M. M., and Fleming, H. P.: *J. Food Sci.*, **54**, 366 (1989)
8) Kuwahara, Y., Otsuka, N., and Manabe, M.: *Nippon Shokuhin Kogyo Gakkaishi (J. Jpn. Soc. Food Sci. Technol.)*, **35**, 776 (1988)
9) Fuchigami, M., Sasaki, A., Kishigami, Y., and Sanmoto, A.: *Nihon Kasei Gakkaishi (J. Home Econ. Jpn.)*, Relationship Between Pectic Changes and Softening of Scallion Pickles, in press
10) Fuchigami, M. and Okamoto, K.: *Nippon Eiyo Shokuryo Gakkaishi (J. Jpn. Soc. Nutr. Food Sci.)*, **37**, 57 (1984)
11) Fuchigami, M.: *Nihon Kasei Gakkaishi (J. Home Econ. Jpn.)*, **37**, 1029 (1986)
12) Fuchigami, M., Kishigami, Y., and Sasaki, A.: *Nihon Kasei Gakkaishi (J. Home Econ. Jpn.)*, **41**, 749 (1990)
13) Fuchigami, M. and Kishigami, Y.: *Nihon Kasei Gakkaishi (J. Home Econ. Jpn.)*, **42**, No.3(1991), in press.
14) Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F.: *Anal. Chem.*, **28**, 350 (1956)
15) Galambos, J. T.: *Anal. Chem.*, **20**, 262 (1969)
16) Bartolome, L. B. and Hoff, J. C.: *J. Agric. Food Chem.*, **20**, 262 (1972)
17) Kusakabe, I., Kamiyama, Y., and Yasui, T.: *Nihon Nogeikagaku Kaishi (J. Agric. Chem. Soc. Jpn.)*, **51**, 167 (1977)
18) Fuchigami, M.: *J. Food Sci.*, **52**, 1317 (1987)

19) Fuchigami, M.: *Nihon Kasei Gakkaishi (J. Home Econ. Jpn.)*, **42**, No.3(1991), in press.

20) Mankarios, A. T., Hall, M. A., Jarvis, M. C., Threlfall, D. R., and Friend, J.: *Phytochemistry*, **19**, 1731 (1980)

21) Das, N. N., and Das, A., and Mukherjee, A. K.: *Carbohydrate Research*, **56**, 337 (1977)

22) Fuchigami, M.: *J. Food Sci.*, **55**, 739 (1990)

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