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# Pectic Changes in Acid-brined Scallions and Non-brined Scallion Pickles During Storage

Michiko FUCHIGAMI, Yasushi MATSUURA, Atsuko SANMOTO,*
Atsuko SASAKI**, and Yoko KISHIGAMI***

*Sanyo Gakuen Women's Junior College, **Chugoku Junior College,
***Niimi Women's Junior College

## Summary

The relationship between pectic changes and softening of scallion bulbs during storage (acid-brining, non-brined pickling, and pre-brined pickling) for 2 years was investigated. During 6 months of storage, acid-brined scallions and non-brined pickles retained their firmness, but they softened rapidly after 1 year. The firmness of scallions and amount of galacturonic acid remaining in the scallions were as follows: acid-brined scallions > non-brined pickles > pre-brined pickles. There was a correlation between the firmness of pickles and the solubilization of pectic substances taken from cell walls. The degree of esterification (DE) of pectic substances decreased rapidly after 2 weeks of acid brining. The activity of pectin methylesterase (PME) in scallion pickles continued to be considerably active even after 1 month of storage. PME affected the demethoxylation of pectic substances in scallion pickles during storage. The DEAE-cellulose column chromatograms and gel filtration profiles of PA and PC after 2 years of storage changed, especially in pre-brined pickles.

## Introduction

Firmness is an important characteristic of pickles, so excessive softening is a common problem. Prior research showed that excessive softening of scallion pickles seemed to be caused by solubilization of cell wall components, particularly the pectic substances.[1)2)] During storage, the DE of pectic substances in scallion pickles decreased.

The objective of the present study was to investigate the relationship between pectic changes and the softening of scallion pickles during storage (acid-brining, non-brined pickling, and pre-brined pickling) for 2 years, and also to investigate the PME activity during storage.

## Material and methods

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

*2) Processing.* Acid-brined scallions: fresh scallions (20 g) were placed into a 30 ml of vinegar-brine (80 g NaCl, 400 ml vinegar and 400 ml water) in a 60 ml glass jar. Pre-brined pickles: the scallions, pre-acid-brined for 2 weeks, were placed into 30 ml of sugar-vinegar solution (150 g sugar and 400 ml vinegar). Non-brined pickles: fresh scallions (20 g) were placed into a 30 ml of sugar-vinegar-brine (15 g NaCl, 150 g sugar and 400 ml vinegar). These pickles were stored at room temperature in 60 ml glass jars. Twelve jars for each sample were prepared.

*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). The experimental results are the average of ten measurements.

*4) Extraction of pectic substances.* This was performed by the same method reported previously.[1)~3)] 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).

*5) Fractionation of pectic substances by DEAE-cellulose column chromatography and gel filtration.* This was performed by the same method reported previously.[4) 5)]

*6) Pectin methylesterase activity.* Pectin methylesterase (PME) activity was measured by a gas chromatography.

## Results and discussion

### *1. Change in firmness of scallion pickles during storage*

Changes in the firmness of pickles (acid brined scallions, pre-brined pickles and non-brined pickles) and the pH level of brines are shown in Fig. 1. Firmness of acid-brined scallions and non-brined pickles slightly decreased after 6 months of storage, but after 1 year, firmness rapidly decreased. After 2 years of storage, acid-brined scallions and non-brined pickles were firmer than pre-brined pickles (which were excessively soft), and brined scallions were the firmest. The pH level of the brine increased after 2 years of storage.

### *2. Change in pectic composition of scallion pickles*

The change in pectic composition of acid-brined scallions and non-brined pickles is shown in Fig. 2 and Fig. 3, respectively. After acid-brining for 2 weeks, the amount of PA decreased, and that of PB increased. This converse tendency continued during 6 months.

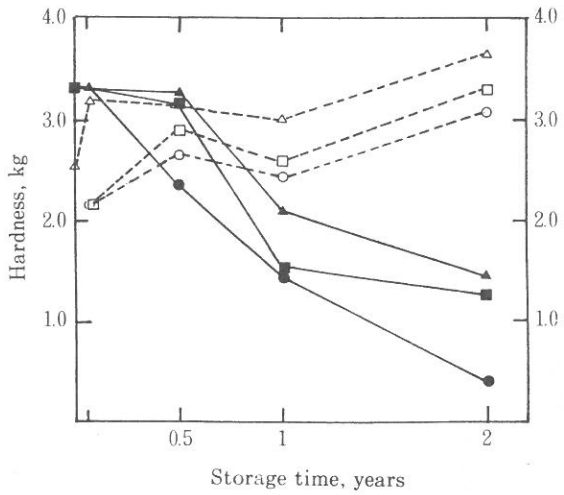


Fig.1. Changes in firmness of scallion pickles and the pH of brine during storage.
▲Hardness of acid-brined scallions.
■Hardness of non-brined pickles.
●Hardness of pre-brined pickles.
△pH of acid-brine.
□pH of sugar-vinegar-brine.
○pH of sugar-vinegar solution.

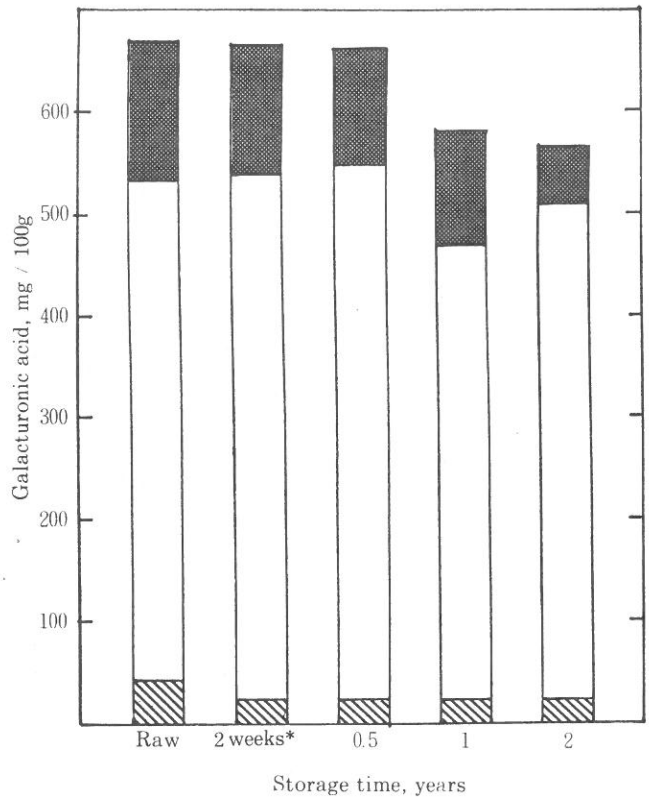


Fig.2. Change in the amount of galacturonic acid in acid-brined scallions during storage.
▨ PA: Extraction with 0.01N HCl (pH 2.0) at 35℃.
□ PB: Residues of PA were extracted with 0.1M sodium acetate buffer solution (pH 4.0) at 35℃.
▩ PC: Residues of pB were extracted with 2% sodium hexametaphosphate solution (pH 4.0) at 90℃.
* Scallion acid-brined for 2 weeks.

By brining, the methoxylation of pectic substances occurred. During 6 months of acid-brining, the scallions maintained their firmness; however, they rapidly softened after 1 year. and the amount of galacturonic acid decreased considerably. The same tendency was observed in non-brined pickles and pre-brined pickles. The firmness of scallions and the amount of galacturonic acid remaining in the scallions were as follows: acid-brined scallions > non-brined pickles > pre-brined pickles. There was a correlation between the firmness of scallion pickles and the solubilization of pectic substances from cell walls.

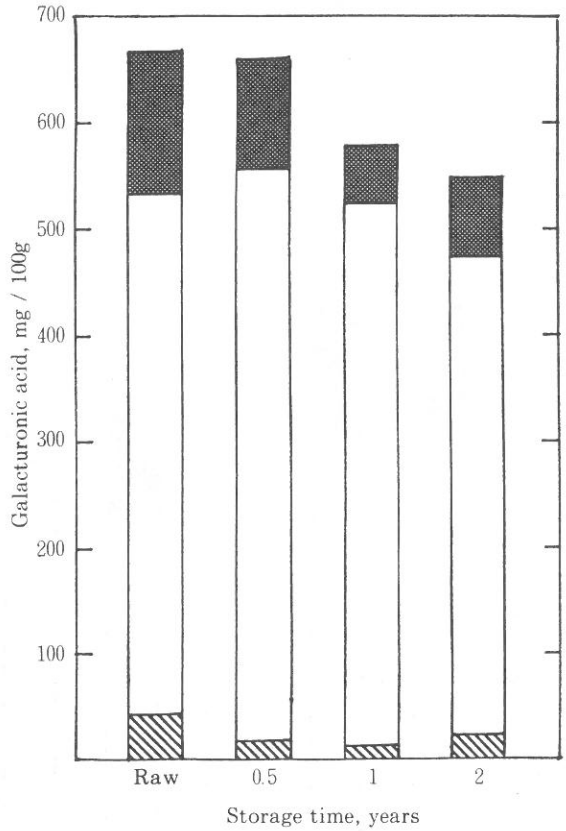


Fig.3. Change in the amount of galacturonic acid in non-brined pickles during storage.
▨ PA, □ PB and ▩ PC: See Fig.2.

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

Change in the DE of pectic substances in acid-brined scallion and non-brined scallion pickles during storage is shown in Fig.4 and Fig.5, respectively. All treatments, such as acid-brining and pickling, reduced the DE of pectic substances in scallions.

*4. Change in pectin methylesterase activity during storage*

Change in pectin methylesterase (PME) activity during acid-brining and pickling is shown in Fig.6. PME activity of raw scallions was 5.0 μmol/min/g tissue. PME activity

increased after 1 day of acid-brining and 3 days of non-brined pickling, and then decreased gradually. However, PME activity continued to be considerable even after 1 month of storage. PME affected the methoxylation of pectic substances in scallion pickles during storage.

*5. Change in DEAE-cellulose 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.7, Fig.8. and Fig.9, respectively. The fractions I, II and III were neutral polysaccharides, weakly acidic polysaccharides (pectin) and pectic acid, respectively[4)5)]

The chromatograms changed during storage, especially in pre-brined pickles. The galacturonic acid of PA in pre-brined pickles was eluted later in fraction II than it was in raw scallions, brined scallions and non-brined pickles (Fig.7). This suggested that PA in pre-brined pickles was more demethoxylated than PA in raw scallions, acid-brined scallions and non-brined pickles.

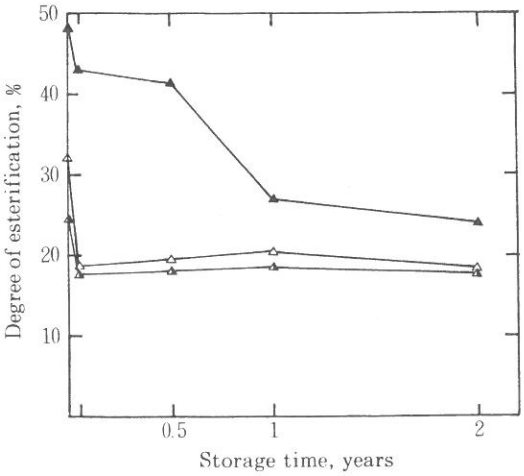


Fig.4. Change in the degree of esterification of pectic substances in acid-brined scallion during storage.
▲PA, ◭PB and △PC: See Fig.2.

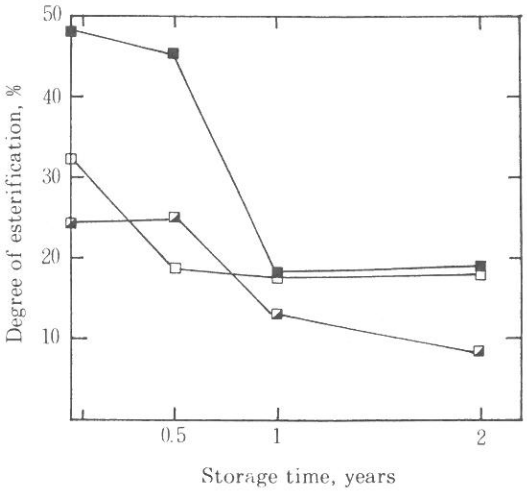


Fig.5. Change in the degree of esterification of pectic substances in non-brined pickles during storage.
■PA, ◪PB and □PC: See Fig.2.

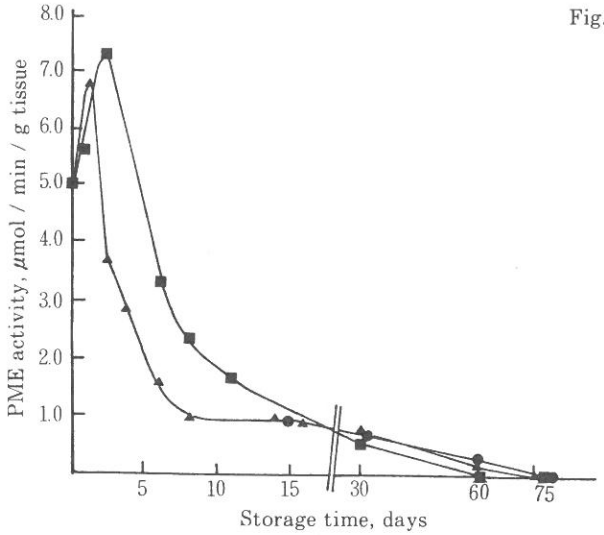


Fig.6. Change in pectin methylesterase activity in scallion pickles during storage.
▲ acid-brined scallions.
■ non-brined pickles.
● pre-brined pickles.

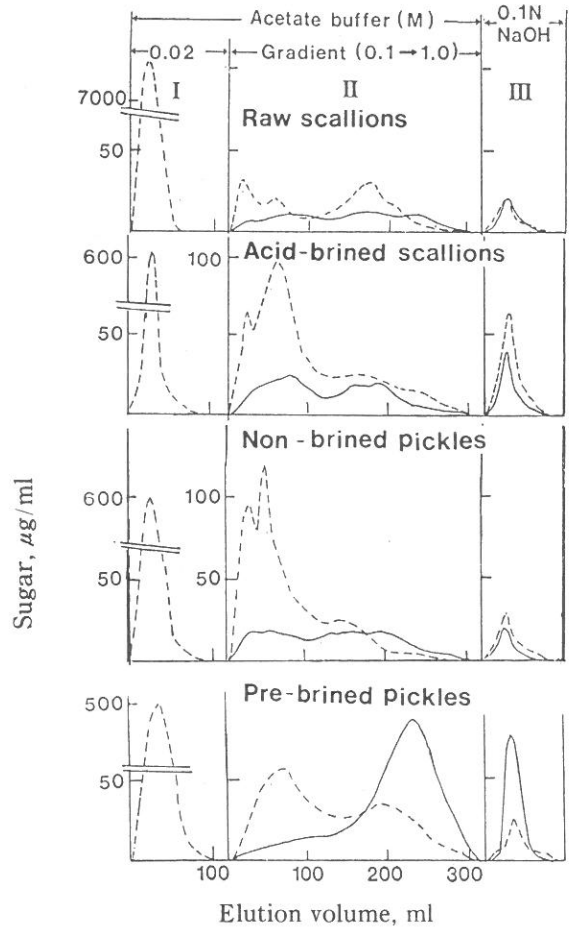


Fig.7. Change in DEAE-cellulose column chromatogram of PA in scallion pickles after 2 years of storage.
— galacturonic acid, ... neutral sugar.

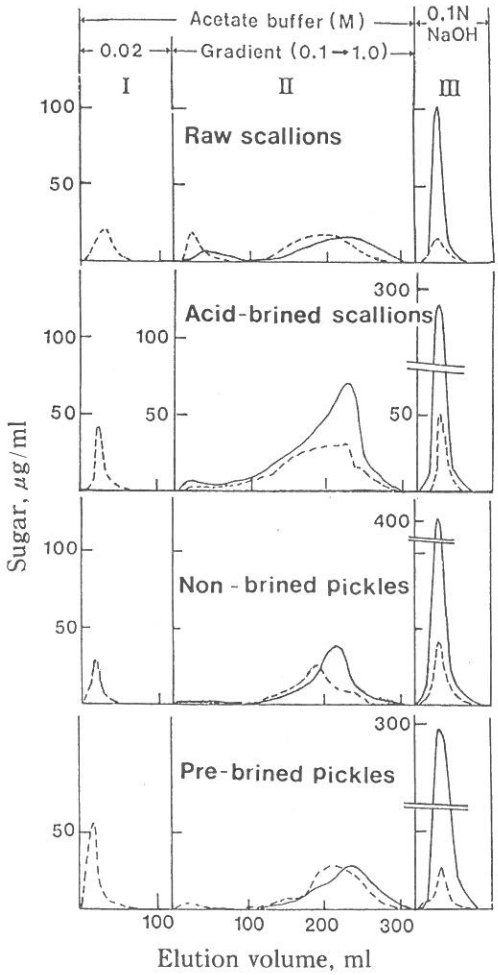


Fig.8. Change in DEAE-cellulose column chromatogram of PB in scallion pickles after 2 years of storage.
– galacturonic acid, ...neutral sugar.

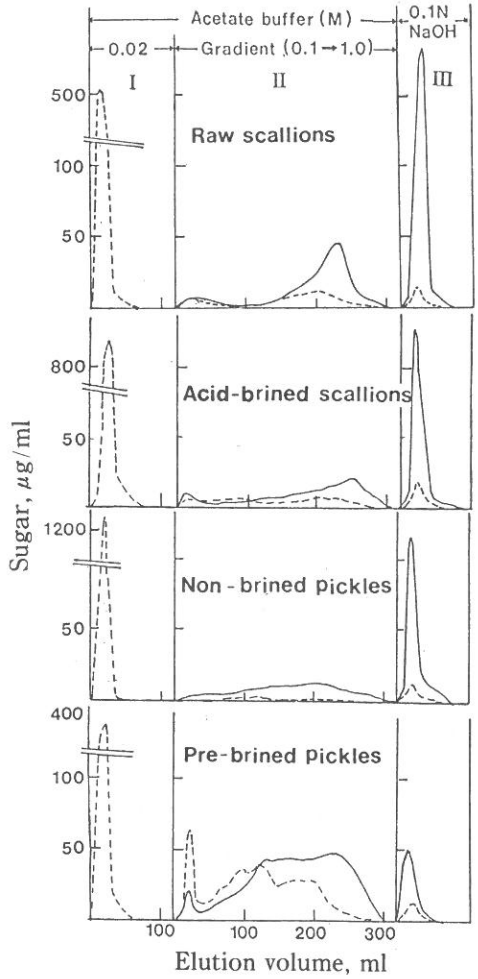


Fig.9. Change in DEAE-cellulose column chromatogram of PC in scallion pickles after 2 years of storage.
—galacturonic acid, ...neutral sugar.

The PB peak was detected at about 230 ml in fraction II of raw and treated scallions (Fig. 8). Since the low methoxyl pectin was usually eluted later in fraction II[4] DE of PB was lower than DE of PA (Fig. 6). 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 DE of PA, although a great change in elution patterns in fraction II of PB was not found during storage.

The uronic acid elution pattern of PC in raw scallions was similar to that of PB. The elution pattern of PC did not change largely during storage of brined and non-brined pickling. However, 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.

*6. 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. 10. 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 pre-brined pickles. The MW of PB did not change after 2 years of storage except for pre-brined pickles, and the MW of PC in non-brined pickles and pre-brined pickles decreased. This shows that MW of the pectic substances in pre-brined pickles decreased greatly. Excessive softening was observed in the pre-brined pickles 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, some of the depolymerized pectic substances remained in the tissues and affected a partial loss of the intercellular cohesion of tissues (especially the pre-brined pickles after 2 years of storage).

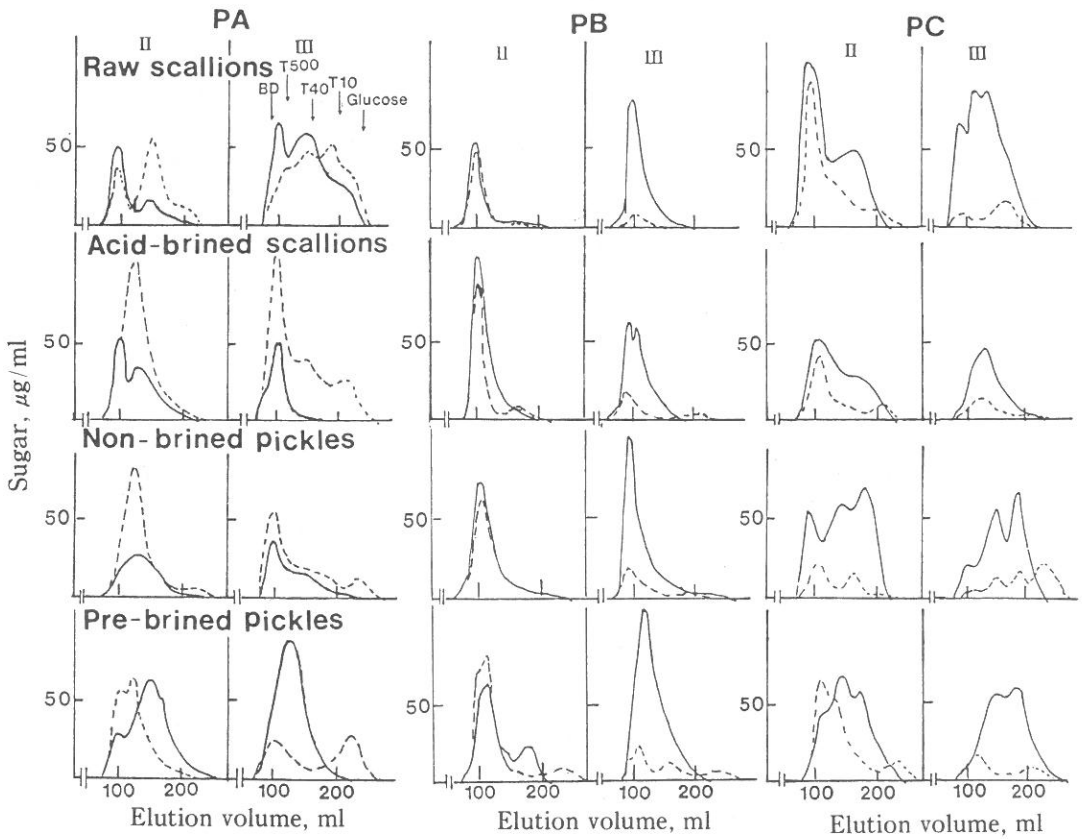


Fig.10. Gel-filtration profile (Sepharose CL-6B) of pectic substances in scallion pickles after 2 years of storage.
PA, PB and PC: See Fig.2.
Ⅱ and Ⅲ: See Fig. 7~9.

The composition of monosaccharides in pectic substances of acid-brined scallions and non-brined pickles after 2 years of storage are shown in Tables 1 and 2, respectively. The main neutral sugar in pectic substances was galactose. The neutral sugar composition did not change greatly during storage.

Table 1. The composition of monosaccharides in neutral and acidic sugars of acid-brined scallions 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 | 0.8 | 29.5 | 0.9 | 0.6 | 68.3 | trace |
| | II | 83.5 | 68.6 | 2.7 | 37.0 | 3.1 | 0.8 | 56.5 | 0 |
| | III | 16.5 | 65.6 | 9.5 | 16.2 | 6.4 | 1.9 | 36.9 | 29.3 |
| PB | I | | 100 | 0 | 12.1 | 7.3 | trace | 80.6 | trace |
| | II | 61.6 | 41.2 | 2.2 | 23.8 | 6.7 | 2.6 | 63.9 | trace |
| | III | 38.4 | 14.6 | 19.7 | 32.8 | 6.5 | 3.6 | 27.8 | 9.6 |
| PC | I | | 100 | 2.8 | 17.5 | 7.0 | 0.7 | 72.0 | 0 |
| | II | 57.5 | 83.1 | 5.1 | 26.2 | 7.6 | 4.6 | 56.5 | 0 |
| | III | 42.5 | 15.5 | 19.7 | 26.0 | 5.6 | 7.2 | 21.3 | 20.3 |

* Fraction obtained by DEAE-cellulose column chromatography (See Fig. 7~9).

** Neutral sugar (%) = neutral sugar ÷ pectic substances (galacturonic acid + neutral sugar) × 100.

Table 2. The composition of monosaccharides in neutral and acidic sugars of non-brined 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 | 5.3 | 23.1 | 0.5 | 1.2 | 69.9 | trace |
| | II | 88.4 | 69.2 | 2.7 | 37.0 | 3.1 | 0.8 | 56.5 | 0 |
| | III | 11.6 | 62.2 | 5.2 | 10.5 | 11.0 | 15.5 | 35.8 | 22.1 |
| PB | I | | 100 | 0 | 21.5 | 0 | 75.7 | trace | 2.9 |
| | II | 43.5 | 43.1 | 3.7 | 4.7 | 6.1 | 1.4 | 84.2 | trace |
| | III | 56.5 | 18.8 | 4.3 | 6.0 | 7.5 | 3.7 | 78.5 | 0 |
| PC | I | | 100 | 0 | 35.9 | 0 | 51.2 | 8.6 | 4.3 |
| | II | 57.3 | 17.3 | trace | 4.7 | 16.8 | 21.2 | 26.4 | 30.8 |
| | III | 42.7 | 12.7 | 19.7 | 26.0 | 5.6 | 7.2 | 21.3 | 20.3 |

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