Effects of Cations and Anions on the Softening of Cooked Japanese Radish Roots and on the Pectic Composition after Cooking

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Disks of Japanese radish roots were cooked in nine salt solutions to investigate the effects of cations (Na+, Mg2+ and Ca2+) and anions (acetate, sulfate and chloride) on the softening of cooked vegetables. As the concentration of CaCl2 (10–1,000 mM) and CaSO4 (0.1–0.25 mM) was increased, the disks became firmer. Conversely, disks cooked in the other salt solutions became softer. The amount of pectic substances remaining in the tissues when the disks were cooked in 0.2 M cooking solutions was (least to greatest) CH3COONa < Na2SO4 < NaCl, (CH3COO)2Mg and (CH3COO)2Ca < MgSO4 < MgCl2 < distilled water < CaSO4 < CaCl2. A clear relationship was found between the firmness of the disks and the amount of pectic substances remaining. As the disks became softer, the amount of water-soluble pectin in the disks increased, and conversely, HC1-soluble pectin and acetate buffer-soluble pectin decreased. The effect of cations on the firmness of the disks was (least to greatest) Na+ < Mg2+ < Ca2+. Sodium and magnesium compounds accelerated the pectic solubilization and softening of the tissues. The effect of anions on the firmness of disks was acetates < sulfates < chlorides, the largest difference being among the calcium compounds. The pH values of the salt solutions were (lowest to highest) chlorides < sulfates < acetates, acetates accelerating pectic solubilization and softening of the tissues due to the high pH level. For these reasons, the presence of both Ca2+ and Cl− in the cooking solution increased the firmness of Japanese radish roots.

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Keywords: Japanese radish root, cooking, softening, anion, cation, pectin.

INTRODUCTION

In a previous paper, the effects of chlorides on the softening of Japanese radish roots was discussed. There was a correlation between the softening of the disks and pectic solubilization. KCl, NaCl and MgCl2 accelerated the pectin solubilization, consequently affecting the softening of the vegetables. CaCl2, AlCl3 and FeCl2 inhibited the pectin solubilization, and hence made the cooked vegetables firmer. Changes in the cell walls of xylem parenchymatous tissues cooked in these solutions were also observed quick-freeze, deep-etching electron microscopy and optical microscopy. These results confirmed that CaCl2 and AlCl3 affected the firmness of cooked Japanese radish roots. Furthermore, there was a greater difference between the effects of solutions of CaCl2 and (CH3COO)2Ca on the softening of Japanese radish roots and potatoes after cooking. This suggested that anions would also affect softening, and anions like citrate, malate, oxalate and phytate decrease the firmness and cellular coherence. Natural salt produced from a salt lake contained NaCl, MgCl2, CaCl2, KCl, CaSO4 and MgSO4, but the effect of sulfates in this salt on the softening of vegetables during cooking was not revealed. For further elucidation, the effects of cations (Na+, Mg2+ and Ca2+) and anions (acetate, sulfate and chloride) on the softening of cooked Japanese radish roots and on pectic solubilization and pectic composition in cooked tissues were then investigated. Changes in the fine structure of the parenchyma cell wall after cooking under the
same condition have already been reported in another paper.5)

**MATERIALS AND METHODS**

1. **Sample preparation**
   Disks were cut from the xylary tissues of Japanese radish roots (*Raphanus sativus* L., cv. Kanpakus) harvested in Okayama prefecture.

2. **Kinds of salts**
   Nine different salts (acetates, sulfates and chlorides of Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\), respectively) were used in this experiment. The concentration of CaSO\(_4\) used was 1/100 unit in comparison with that of the other salts, because CaSO\(_4\) was only slightly soluble in water (the solubility of CaSO\(_4\) was 0.1619 g/100 g of water at 100°C).

3. **Cooking procedure and measurement of tissue firmness**
   A) Five gram disks (5 mm thick and 10 mm in diameter) were dropped into boiling distilled water and 0.01–1.0 \(\text{m}\) salt solutions (100 ml) in a conical beaker (200 ml). After cooking for 15 min, the firmness of each disk was measured with a rheometer (Fudo NRM-2002J). After cooking in 0.2 \(\text{m}\) salt solutions by the same procedure, the pectic substances in the disks were extracted, and galacturonic acid was then determined by using the same method as that reported in the previous paper.2) The amounts of cations in each fraction were determined by atomic absorption spectrophotometry.

   B) Radish disks (10 mm thick and 21 mm in diameter) were cooked in distilled water and 0.2 \(\text{m}\) salt solutions (1,000 ml) for 30 min. The firmness of the surfaces and inner parts of the disks was then measured.9)

**RESULTS**

1. **Effect of cation and anion concentration on the softening of cooked Japanese radish roots**
   The firmness of Japanese radish roots cooked in various salt solutions for 15 min by cooking procedure A is shown in Fig. 1. Disks cooked with CaCl\(_2\) and CaSO\(_4\) were firmer than those cooked in distilled water. Conversely, those cooked with magnesium compounds and (CH\(_3\)COO)\(_2\)Ca were slightly softer than those cooked in distilled water, while those cooked with sodium compounds were the softest.

   As the concentration of the CaCl\(_2\) and CaSO\(_4\) solutions was increased (from 10 mm to 1,000 mm and from 0.1 to 0.25 mm, respectively), the disks became firmer. Conversely, the disks cooked in the other salt solutions became softer. The difference in effect of anions on the softening of disks was greatest among the calcium compounds, and the degree of firmness of the disks (from high to low) was chloride>sulfate>acetate. The pH values of the salt solutions were (from lowest to highest) chloride<sulfate<acetate (Table 1). As the concentration of salts was increased, the pH values of the chloride solutions decreased, and conversely, those of the acetate solutions increased.

   The firmness of roots cooked with the sodium and magnesium compounds decreased with increasing concentration of the salts, in spite of a slight fall of pH with the chlorides and sulfates. This suggests that the amounts of Na\(^+\) and Mg\(^{2+}\) played a larger role in reducing the texture than those of the anions (pH) in the sodium and magnesium compounds.
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2. Effects of cations and anions on pectic solubilization and pectic composition

The firmness of Japanese radish roots cooked for 15 min in 0.2 M salt solutions is shown in Fig. 2. The compositions of the pectic substances which were successively extracted from the alcohol-insoluble solids (AIS) of raw and cooked roots are shown in Fig. 3. When cooked in the various salt solutions, the firmness of Japanese radish roots was (from soft to firm) Na₂SO₄, CH₃COONa < NaCl, (CH₃COO)₂Mg, MgSO₄ and (CH₃COO)₂Ca < MgCl₂ < distilled water and CaSO₄ < CaCl₂. The pectic substances remaining in tissues was (in increasing amount) CH₃COONa < Na₂SO₄ < NaCl, (CH₃COO)₂Mg and (CH₃COO)₂Ca < MgSO₄ < MgCl₂ < distilled water < CaSO₄ < CaCl₂, Na⁺ < Mg²⁺ < Ca²⁺, and acetates < sulfates < chlorides. There was a clear relationship between the firmness of the cooked roots and the amount of pectic substances remaining. Sodium and magnesium compounds and (CH₃COO)₂Ca accelerated pectic solubilization and softening of the tissues, while CaCl₂ and CaSO₄ inhibited them. The presence of both Ca²⁺ and Cl⁻ in the cooking solution increased the firmness.

The amount of water-soluble pectin (WSP) in the raw roots was particularly small, but it was increased by cooking, the amount of WSP being (greatest to least) Na⁺ > Mg²⁺ > Ca²⁺, and ace-

Table 1. pH values of various salt solutions after cooking for 15 min

<table>
<thead>
<tr>
<th></th>
<th>10 mM</th>
<th>25 mM</th>
<th>50 mM</th>
<th>100 mM</th>
<th>250 mM</th>
<th>1,000 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>6.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃COONa</td>
<td>6.68</td>
<td>6.85</td>
<td>6.99</td>
<td>7.13</td>
<td>7.33</td>
<td>7.71</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>6.23</td>
<td>6.14</td>
<td>6.00</td>
<td>5.97</td>
<td>5.94</td>
<td>5.81</td>
</tr>
<tr>
<td>NaCl</td>
<td>6.21</td>
<td>6.18</td>
<td>6.16</td>
<td>6.08</td>
<td>5.97</td>
<td>5.73</td>
</tr>
<tr>
<td>(CH₃COO)₂Mg</td>
<td>6.41</td>
<td>6.52</td>
<td>6.64</td>
<td>6.71</td>
<td>6.84</td>
<td>6.86</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>6.57</td>
<td>6.45</td>
<td>6.33</td>
<td>6.28</td>
<td>6.16</td>
<td>5.32</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>6.32</td>
<td>6.14</td>
<td>5.90</td>
<td>5.62</td>
<td>5.28</td>
<td>5.12</td>
</tr>
<tr>
<td>(CH₃COO)₂Ca</td>
<td>6.59</td>
<td>6.71</td>
<td>6.71</td>
<td>6.78</td>
<td>6.80</td>
<td>6.94</td>
</tr>
<tr>
<td>CaSO₄*</td>
<td>6.24</td>
<td>6.24</td>
<td>6.23</td>
<td>6.28</td>
<td>6.30</td>
<td>6.30</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>6.03</td>
<td>5.83</td>
<td>5.78</td>
<td>5.71</td>
<td>5.66</td>
<td>5.42</td>
</tr>
</tbody>
</table>

* The concentration of CaSO₄ was 1/100 unit in comparison with that of the other salts.

![Fig. 2](image-url) Changes in the firmness of Japanese radish roots cooked for 15 min in various 0.2 M salt solutions

![Fig. 3](image-url) Changes in the composition of pectic substances in Japanese radish roots cooked for 15 min in various 0.2 M salt solutions

- **WSP**: water-soluble pectin extracted from AIS by soaking in distilled water for 24 h (8 h + 16 h) at 20°C,
- **PA**: extracted from the residue after extracting WSP with 0.01 n HCl (pH 2.0) at 35°C for 24 h × 4 times,
- **PB**: extracted from the residue after extracting PA with a 0.1 M acetate buffer (pH 4.0) at 35°C for 24 h × 3 times,
- **PC**: extracted from the residue after extracting PB with a 2% sodium hexametaphosphate solution (pH 4.0) at 90°C for 3.5 h × 4 times,
- **PD**: extracted from the residue after extracting PC with 0.05 n HCl at 90°C for 2 h × 2 times.

The amounts of WSP and pectic substances released into the cooking solutions showed the same trend. These pectic substances were depolymerized by transelimination, and part of them (low molecular weight) was released into the cooking solution. The rest remained in the tissues. When the roots were cooked with Na\(^+\) and Mg\(^{2+}\), the pectic substances which were insoluble and stable due to Ca\(^{2+}\) were more easily extracted. The cause of this seems to have been an exchange of Ca\(^{2+}\) in the tissues, and of Na\(^+\) and Mg\(^{2+}\) in the cooking solution. The roots cooked in the Na\(^+\) solutions were the softest, and this suggests that the substitution reaction of Na\(^+\) was stronger than that of Mg\(^{2+}\).

The amount of PA (0.01 N HCl-soluble pectin; high-methoxyl pectin) was Na\(^+\)<Mg\(^{2+}\)<Ca\(^{2+}\), and acetates<sulfates<chlorides. When the disks were cooked with CaC\(_2\) and CaSO\(_4\), considerable amounts of PA remained in the tissues; therefore, these tissues stayed firm. The amount of PA decreased as that of WSP increased. PA which was difficult to extract in water was extracted by using a diluted HCl solution (calcium and other metal chelating agents). Almost all the magnesium and calcium in AIS was extracted with the 0.01 N HCl solution. Pectic substances remaining after the removal of Ca\(^{2+}\) and Mg\(^{2+}\) were PB, PC and PD, which were precipitated at pH 2.

The amount of PB (0.1 M acetate buffer-soluble pectin; low-methoxyl pectin) was Na\(^+\)<Mg\(^{2+}\)<Ca\(^{2+}\), and acetates<sulfates<chlorides. When the roots were cooked with CaSO\(_4\), the amount of WSP was small, and conversely, that of PB was large. The amounts of PC and PD in the cooked roots were comparatively small, and there was no significant difference found among them.

The pH values of the solutions after cooking are shown in Table 2, the pH values of the acetate solutions being higher than that of distilled water. These high pH values affected the softening of those roots cooked in the acetate solutions. The pH values of the chloride and sulfate solutions were lower than that of distilled water.

**3. Effects of cations and anions on the firmness of the surface and the inner parts of Japanese radish roots after cooking**

The firmness of the surface and inner parts of Japanese radish roots cooked in 0.2 M chloride solutions for 15 min and 30 min is shown in Fig. 4. The surface of the disks cooked with CaC\(_2\) and CaSO\(_4\) was firmer than the surface of disks cooked in distilled water. Conversely, the surface of disks cooked with the other salts was softer than those cooked in distilled water.

When Japanese radish roots were cooked in distilled water, CaC\(_2\) and CaSO\(_4\) solutions for 15

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Table 2. pH values of 0.2 M salt solutions after cooking for 15 min

<table>
<thead>
<tr>
<th>Salt</th>
<th>pH Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)COONa</td>
<td>7.43</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>5.86</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.84</td>
</tr>
<tr>
<td>Distilled water</td>
<td>6.55</td>
</tr>
</tbody>
</table>

*2 mm CaSO\(_4\).*

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Fig. 4. Firmness of Japanese radish roots cooked for 30 min in various 0.2 M salt solutions

- Surface, Inner parts.
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min or 30 min, the surface of the disks was firmer than the inner parts. Conversely, when the disks were cooked in the other salt solutions, the surface softened more rapidly than the inner parts. The firmness of disks cooked in the various cations and anions was (softest to firmest) Na\(^+\) < Mg\(^{2+}\) < Ca\(^{2+}\), and acetates < sulfates < chlorides. These results agree with the results of the pectic analysis and observations on the fine structure of the parenchyma cell wall.\(^5\)

**DISCUSSION**

Japanese radish roots cooked in various salt solutions (acetates, sulfate and chlorides of Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\)) resulted in the firmness of the roots being (softest to firmest) Na\(^+\) < Mg\(^{2+}\) < Ca\(^{2+}\), and acetates < sulfates < chlorides. The amount of pectic substances remaining in the tissues was (least to greatest) Na\(^+\) < Mg\(^{2+}\) < Ca\(^{2+}\), and acetates < sulfates < chlorides. The effect of anions on the softening of roots and on the pectic solubilization seemed to be related to the pH value. When vegetables were cooked in weakly acidic solutions, they maintained their firmness.\(^7\) The pH values of the chloride solutions were lower than those of the acetate and sulfate solutions. Therefore, the roots cooked with chloride compounds were firmer than those cooked with sulfate and acetate compounds. With the calcium compounds, the effect of anions was the greatest. Sodium and magnesium ions accelerated the solubilization of calcium ions and pectic substances, resulting in considerable softening of the roots. Therefore, the effects of anions in sodium and magnesium compounds on the texture of the roots were less than those of the calcium compounds. As the concentration of chlorides and sulfates of Na\(^+\) and Mg\(^{2+}\) was increased, their pH values decreased, and the cooked roots became softer. These results suggest that, for sodium and magnesium, the amounts of cations had a greater affect on the softening of cooked roots than the amounts of anions and the pH values did.

CaCl\(_2\) has often been used to provide firm cooked vegetables and fruits. In a previous paper,\(^9\) roots cooked in a mixed solution of CaSO\(_4\) and NaCl became firmer than those cooked in a CaSO\(_4\) solution. The presence of both Ca\(^{2+}\) and Cl\(^-\) in the cooking solution greatly increased the firmness.

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**REFERENCES**


**ダイコンの煮熟軟化とベクチン組成の変化に及ぼす陽イオン、陰イオンの影響**

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平成5年2月15日受理

煮熟野菜の軟化に及ぼす陽イオン（ナトリウム, マグネシウム, カルシウム）と陰イオン（酢酸, 硫酸, 塩化物）の影響を検討するために, ダイコンの円盤を9種類の塩溶液中で煮熟した. 塩濃度が増すに従って塩化カルシウム (10〜1,000 mM), 硫酸カルシウム (0.1〜0.25 mM) では硬さが著しく, 反対にその他の塩類では軟化した. 以下の0.2 M溶液中で煮熟したとき, 沸騰中に残存したベクチン量は, 酢酸ナトリウム < 硫酸ナトリウム < 食塩, 酢酸マグネシウム, 酢酸カルシウム < 硫酸マグネシウム < 塩化マグネシウム < 塩化カルシウム < 蒸留水 < 硫酸カルシウム < 塩化カルシウムの順に多かった. 煮熟
後の円盤の硬さとペクチン質の残存量の間に相関があった。円盤が柔らかいほど、組織中の水溶性ペクチンが多く、反対に希塩酸可溶性ペクチンや酢酸塩緩衝液可溶性ペクチンが少なかった。円盤の硬さへの陽イオンの影響は、$Na^+ < Mg^{2+} < Ca^{2+}$ の順に大であった。ナトリウム、マグネシウム塩はペクチン質の溶出と組織の軟化を促進した。円盤の硬さへの陰イオンの影響は、塩酸塩と硫酸塩の酸化物の順に大で、カルシウム塩において最も大きな違いがみられた。塩類溶液の pH は塩化物と硫酸塩の酸化物の順に高く、酢酸塩は pH が高いためにペクチン質の溶出と軟化を促進した。煮汁中に $Ca^{2+}$ と $Cl^-$ が存在すると硬さが著しく増した。

キーワード：ダイコン，煮熟，軟化，アニオン，カチオン，ペクチン。