Effects of Ascorbic Acid and Related Compounds on Wheat Flour Dough and Starch in Breadmaking

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The addition of L-ascorbic acid (AsA) or dehydroascorbic acid (DHA) to wheat flour lowered the gelatinization temperature of starch about 2°C, and reduced the gelatinization enthalpy about 10% in comparison with that of the control or D-AsA. Farinography of wheat flour dough added with AsA or DHA showed a shorter development time than that with 2,3-diketogulonic acid or the control, probably by the formation of SS cross-linkages of gluten molecules. Scanning electron microscopic observations of wheat dough after 25-min mixing with AsA or DHA suggested the changes in the rigidity of dough, followed by some changes in the wrapping of gluten to the starch granules. Considering these results, we discuss the changes of gelatinization temperature, enthalpy, gluten, and SH contents after addition of AsA and related compounds to wheat flour.

L-Ascorbic acid (AsA) is widely used as an improver for breadmaking instead of potassium bromate. AsA is easily oxidized to dehydroascorbic acid (DHA) in neutral aqueous solutions in the presence of oxygen. DHA derived from AsA by AsA oxidase, air oxidation, UV light, and metal ions oxidizes SH groups of gluten molecules in dough. When SH groups are oxidized to SS linkages during the mechanical mixing of dough, some changes in wrapping of starch with gluten may be considered. Also, network gluten structures thus formed containing SS linkages, result in the holding of a favorable amount of gas in the crumb of the bread baked. From this point of view, we intend to understand some changes in dough, such as gelatinization temperature, number of SH groups, dough strength studied by farinography, and scanning electron microscopic observation.

MATERIALS AND METHODS

Materials. Wheat flour used in this study was the brand name “Hermes” made by Okumoto Flour Milling Co., Ltd. from Western Red Spring and Hard Red Spring or Winter. The protein contents was 11.8% and ash was 0.38% at 11.8% moisture. Dry baker’s yeast used was kindly donated from the Toyo Jozo Co., Ltd. DHA and 2, 3-diketogulonic acid (DKG) were prepared from AsA, as reported. Other reagents were of analytical grade, unless otherwise stated.

Preparation of dough by sponge-and-dough method. Wheat flour (280 g), sucrose (17 g), and NaCl (5 g) were mixed in a polyethylene bag. The mixed materials and 210 g of water containing 14 mg (50 ppm) of AsA, DHA or DKG were mixed in a pancase. Bread was made in an automatic breadmaker sold as “home bakery” for domestic use (SD-BT3, Matsushita.
Analytical method. For farinography with a Brabender farinograph, wheat flour (300 g) and distilled water (180 g) were used.

The SH and SS contents were determined by the methods of Obata et al.\textsuperscript{16} and Cavallini et al.,\textsuperscript{17} respectively. The data obtained were applied to determine significance of difference between means.\textsuperscript{18}

Differential scanning calorimetry (DSC)\textsuperscript{19,20}

DSC was done with a Seiko DSC SSC-560S calorimeter. As the dough sample for DSC, 20 mg of each dough was used. The reference pan contained 8 mg of liquid paraffin. The temperature was raised at the rate of 8.1°C/min, with a sensitivity of 0.04 mcal/sec. The range of the scanned temperature was approximately 16-120°C. All samples were run in duplicate at least. The DSC apparatus was calibrated with the melting enthalpy of indium.

For the reference of DSC measurement without mixing, 4 mg of wheat starch (moisture 11.0%) and 10 µl of deionized water containing a given amount of AsA or related compounds were used.

Scanning electron microscopic (SEM) observation. SEM observation was performed as reported by Nihei et al.\textsuperscript{21} with a slight modification. Hitachi scanning electron micrographic apparatus model S-800 was used.

RESULTS AND DISCUSSION

SEM of wheat dough

Figure 1 shows the results of SEM of dough sample containing 50 ppm of AsA or DHA. Most of the starch granules in the control dough were uniformly covered with gluten molecules.\textsuperscript{22} So, the surfaces of both the large primary and small secondary starch granules looked quite smooth. However, gluten molecules tended to take rod-like or filamentous forms by the addition of AsA or DHA (as shown by arrows).\textsuperscript{23} Furthermore, most of the large primary starch granules seemed to be uncovered with gluten. That is, gluten tended to be separated from the surface of the starch granule, because of the tendency of the solidification of the gluten.

Since AsA or DHA oxidized SHH groups of gluten molecules as reported previously,\textsuperscript{14} gluten molecules seemed to become more rigid and hydrophobic than without the additives. The amounts of free SH groups in the gluten were not large, but some characteristic changes of gluten added with AsA or DHA were distinct compared with the control sample.

![SEM images of dough samples](image-url)
Ascorbic Acid Related Compounds on Dough and Starch in Breadmaking

Effects of AsA, DHA, and DKG on the changes of wheat dough in farinogram

Farinography of dough containing AsA, DHA or DKG was tested (Fig. 2). When the farinograms of AsA or DHA were compared with those of DKG or control, the development times of AsA, DHA, DKG and the control in the farinogram were about 4, 5, 7, and 7 min, respectively. Therefore, the pattern of the farinograms of AsA or DHA was similar to that of DKG or control. And the development time of AsA or DHA became faster than DKG or control. This may be caused by the immediate formation of SS cross-linkages from SH groups in the dough gluten. The formation of rigid gluten might decrease the development time. The addition of DKG gave almost similar farinogram to the control. Therefore, DKG, the hydrolyzed form of lactone ring of DHA, did not show any improving effect on dough.

Effects of additives on the temperature of starch gelatinization and SH content in wheat flour dough

The gelatinization temperature of starch in wheat dough was tested by DSC just before the addition of dry yeast. Addition of AsA or DHA (50 ppm each) lowered the peak temperature of gelatinization about 2°C compared with the control (Table 1). However, the dough with DKG had almost the same gelatinization temperature as that of the control dough (data not shown). The D-form of AsA did not affect the gelatinization temperature or the enthalpy change, differently from L-AsA or DHA. This suggests that D-AsA may have no positive oxidation effect on the SH groups in gluten, as reported already. The lowering of the gelatinization temperature may be closely related to the wrapping of starch that granules with gluten molecules. These results may indicate large primary starch granules which were not covered with gluten molecules may lower the gelatinization temperature.

Table 1. Summary of gelatinization temperature of wheat flour dough.

<table>
<thead>
<tr>
<th>Wheat flour dough</th>
<th>$T_o$</th>
<th>$T_p$</th>
<th>$T_f$</th>
<th>$\Delta h$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>°C</td>
<td>°C</td>
<td>(mcal/mg)</td>
</tr>
<tr>
<td>Control</td>
<td>59.0</td>
<td>82.0</td>
<td>106.0</td>
<td>2.10</td>
</tr>
<tr>
<td>L-AsA</td>
<td>59.0</td>
<td>80.0</td>
<td>103.0</td>
<td>1.88</td>
</tr>
<tr>
<td>DHA</td>
<td>59.0</td>
<td>80.0</td>
<td>103.0</td>
<td>1.87</td>
</tr>
<tr>
<td>D-AsA</td>
<td>58.9</td>
<td>82.2</td>
<td>106.1</td>
<td>2.09</td>
</tr>
</tbody>
</table>

$T_o$, Onset temp.; $T_p$, Peak temp.; $T_f$, Final temp.

Table 2. Effects of AsA and related compounds on SH in flour.

<table>
<thead>
<tr>
<th>SH Contents (10^{-7} eq/g flour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No mixing</td>
</tr>
<tr>
<td>Mixing (25 min)</td>
</tr>
<tr>
<td>Control</td>
</tr>
<tr>
<td>AsA 50 ppm</td>
</tr>
<tr>
<td>DHA 50 ppm</td>
</tr>
<tr>
<td>DKG 50 ppm</td>
</tr>
</tbody>
</table>

Values are the means±SD of 6 experiments.
also found for the control.

Considering the pattern of farinogram, the decrease in SH content, the lowering of gelatinization temperature of starch in dough, and the change of SEM observation, we may conclude as follows. During the process of dough mixing, AsA was oxidized to DHA, and the resulting DHA oxidized the SH groups to SS cross-linkages. In the course of the formation of SS cross-linkages, the gluten molecules would not wrap large pieces of primary starch, probably because of the increasing rigidity of the gluten. The SEM observation showed a change of gluten molecules from a viscous state to a filamentous state. Therefore, the lowerings of the starch gelatinization temperature and reduction of enthalpy were about 2°C and 10%, respectively. These results may be caused by the change of wrapping of gluten molecules on the surface of starch granules, since the oxidation of SH groups would make the network structure of gluten more rigid. The addition of a small amount of AsA or DHA improved the loaf volume of bread baked by “home bakery”\(^4\). But, an excess amount (more than 50 ppm) of AsA or DHA reduced the loaf volume, as the result of overoxidation of SH groups in gluten. These results suggest that a small amount of AsA oxidizes the SH groups in the dough, followed by the formation of favorable network structures. However, the addition of an excess amount of AsA or DHA changes the properties of dough unfavorably, probably towards to negative changes of wrapping of gluten to the surface of starch granules or rigidity of the dough. Thus, the formation of cross-linkage of gluten due to SS-linkage formation is potentially important for breadmaking.

The authors are much indebted to Prof. Dr. S. Matsumoto, University of Osaka Prefecture, for his helpful discussion. We are grateful to Prof. T. Mita, Osaka Women’s University for the use of Farinograph and his helpful discussion. We thank the Okamoto Flour Milling Co., Ltd. for supplying wheat flour, and the Toyo Jozo Co., Ltd. for providing dry yeast. This study was supported in part by a Grant for Scientific Research from the Fuji-Elizabeth Arnold Foundation.

REFERENCES

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(Received December 20, 1990;
accepted March 27, 1992)

製パン中においてアスコルビン酸関連化合物の小麦粉ドウおよび澱粉に及ぼす効果について

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L-アスコルビン酸（AsA）およびデヒドロアスコルビン酸（DHA）を製パン材料に加えてミキシングするとコントロールまたは D-AsA を添加したものに比べ澱粉の糊化温度が 2℃、糊化エンタルピーが約 10% 減少した。AsA あるいは DHA を加えた小麦粉ドウのファリノグラフでは 2,3-ジヒドロアスコルビン酸あるいは無添加のものに比べ、グレゼ分子の SS 結合の形成のためにドウのデベロップ時間が短かくなった。さらに、25 分間ミキシングした試料の走査電顕観察の結果、ドウはよりリッチドになり、澱粉粒へのグルテンの包込みに変化が見られた。これらの結果をもとにして小麦粉に AsA 関連化合物を添加した場合の糊化温度、グルテン、SH 含量の変化等について考察した。