OXIDASE AND CATALASE ACTIVITY OF BARTLETT PEARS IN RELATION TO MATURITY AND STORAGE

By Boyce D. Ezell, assistant horticulturist, and Fisk Gerhardt, physiologist, Division of Fruit and Vegetable Crops and Diseases, Bureau of Plant Industry, United States Department of Agriculture

INTRODUCTION

In a previous publication (3) it was pointed out that Bartlett pears picked relatively immature gave a less desirable canned product than did those left on the tree until more mature. The less mature fruit tended to have a pale orange-yellow color in contrast to the clear translucent cream color of the more mature fruit. This difference in color was due to changes in the fruit itself and not to differences in processing. It was found that for best results Bartlett pears should be harvested at a pressure test of 17 to 15 pounds (as measured on the pared flesh by means of the United States Department of Agriculture pressure tester with the 5/16-inch plunger) and stored immediately at 30° to 32° F. for 15 to 30 days. Longer periods in cold storage tended to exaggerate the undesirable color of the less mature fruit.

An oxidase is believed to be the principal agent responsible for the darkening of pears in preparation for canning. In commercial canneries the pared fruit is placed in a sodium chloride solution to inactivate the enzyme and prevent excessive oxidation until the fruit is ready for processing. If the oxidase is very active the darkening will be rapid and the fruit may be discolored before it can be placed in the brine solution, or the enzyme may not be completely inactivated and the darkening may continue while the fruit is being graded and placed in the can.

The work reported herein was undertaken in the hope that information might be obtained on the oxidase and catalase activity of Bartlett pears that would be of value in reducing the wide variations in color in the canned fruit. The investigations were made at Wenatchee, Wash., during the 1935 and 1936 seasons.

REVIEW OF LITERATURE

In the study of the physiological development and storage of fruits, catalase has been used more often than oxidase to indicate metabolic changes; consequently the literature dealing with catalase is much more voluminous. However, oxidase activity probably plays a more important part in the discoloration of fruit during canning operations and is therefore of greater interest from the standpoint of food processing.

Ajon (1), working with citrus fruits, reported that as the fruit ripened the oxidase gradually diminished from the center of the parenchyma outward to the periphery, finally almost, if not quite,

1 Received for publication August 18, 1937; issued April 1938.
2 Reference is made by number (italic) to Literature Cited, p. 345.
disappearing. De Villiers (2) also reported a decrease in oxidase activity of the grape as the berry ripened. Catalase increased with maturity but decreased slightly with final stages of maturation.

Haber (7) found greater oxidase activity in ripe tomato fruits than in green ones; catalase activity, on the other hand, was greater in green mature fruits. Gustafson et al. (5) reported a slightly lower catalase activity in yellow-orange and orange-colored tomatoes than in orange-red and red ones.

Lüers et al. (11) found that barley increased in catalase content during ripening until it became yellow, after which it decreased while the resting state was attained. During storage there was no change in the catalase content. Noguchi (13) reported a gradual decrease, without any sudden change at any time, in the catalase content of rice stored for 18 months. The oxidase content was unchanged.

Neller (12) found that in apples free from break-down catalase tended to increase during the earlier, then to decrease during later periods of storage, corresponding to the youth and senescence of the fruit. Harding (8) found that under cold-storage conditions an increase in catalase activity of Grimes Golden apples was a fairly accurate index to the approach of soggy break-down. Overholser (14) found that catalase decreased in Bartlett pears as maturity advanced and that “the effect of the storage temperature upon catalase activity depended upon the duration of the storage period, which varied with the temperature.” Storage at 0°C. for 6 months resulted in greater activity in four varieties of pears. Reed (15) reported no catalase in green pineapples, some in hard yellow ones, and more in fully ripe ones.

In studies of the effect of maturity and storage on the oxidase and catalase activity of apples, Hinton (10) found that oxidase activity decreased during ripening on the tree, and markedly but slowly during storage. Catalase increased during storage, but in some cases decreased during the later stages. The rate of increase was highest during the early part of storage and fell more or less rapidly during the storage period. The later the date of picking the higher was the early rate of increase and the steeper the subsequent fall. With fruit picked at three stages of maturity the catalase activity was lowest in the middle picking. Hinton thought that this was probably due to lower temperatures prevailing prior to the second picking.

**METHODS OF PROCEDURE**

None of the fruit used in the present tests was canned. In order to make it possible to correlate oxidase and catalase activity with the previously observed behavior of the canned product, maturity and handling of the various lots of pears were similar to those reported in a previous paper (3). The oxidase activity was determined iodo-metrically as described by Guthrie (6) and is reported as cubic centimeters of N/100 sodium thiosulphate per 10 cc of juice, except as noted in the text. Catalase activity was determined by a water-displacement method similar to that described by Heinicke (9) and is reported as cubic centimeters of oxygen liberated in 5 minutes by 1 cc of juice. All enzyme determinations were made on the unripened fruit. Preliminary determinations made on the unripened fruit in storage at
32° F. and at daily intervals during ripening at 65° showed that the enzyme activity varied with the degree of ripeness. At the optimum stage for canning, oxidase activity was slightly greater than during storage at 32°, while catalase activity, which often increased at first, had fallen below that of the unripened fruit. In order to insure uniformity of sampling, unripened fruit was used. The methods of procedure have been described in detail by the authors in another paper (4).

EXPERIMENTAL DATA

EFFECT OF MATURITY ON ENZYME ACTIVITY

Bartlett pears were harvested at three stages of maturity, from three localities, and stored immediately at 32° F. Samples from each of the three localities were taken on the same dates, but owing to differences in elevation and soil conditions, the stages of maturity were not comparable. Oxidase and catalase determinations were made at harvest and at intervals during storage.

A very strong positive correlation was found between maturity, as measured by the pressure test, and oxidase activity, as is shown in figure 1. The pressure readings of the fruit during harvest ranged from 20.3 to 13.2 pounds, a drop of 35 percent, while the oxidase activity ranged from 32.8 to 7.9 cc of sodium thiosulphate, a drop of 76 percent.

No correlation was evident between degree of maturity, as measured by the pressure test, and catalase activity when the nine lots were arranged according to decreasing pressure. However, as shown in figure 2, when the lots were arranged by orchards the catalase activity
was low at the second picking and higher at the first and third pickings for two orchards. In the third orchard, in which the pressure reading was down to 16.5 pounds at the first picking, the catalase was low and continued to increase in the later pickings, which is in agreement with the hypothesis that catalase probably decreases as maturity advances, up to a definite stage, and then increases.

**ORCHARD LOCATION AND ENZYME ACTIVITY**

The orchards from which the pears used in the maturity studies were taken represent different growing conditions. Orchard F is a sandy loam, and fruit grown on this type of soil matures earlier than fruit grown on the type represented by orchard V, a medium-heavy loam more nearly typical of Wenatchee Valley orchards. Orchard B is also a medium-heavy loam but is situated at an elevation approximating 2,400 feet, whereas the elevation of the other two orchards is only 850 feet.

While the pears from the three orchards were not exactly comparable in maturity, there appear to be greater differences in enzyme activity than would be expected from maturity differences alone. For each pound drop in pressure there was an average drop in oxidase activity of 2.7 cc, 3.0 cc, and 3.8 cc in orchards F, V, and B, respectively, the greatest drop being in the least mature fruit. If the third picking of orchard B is compared with the first picking of orchard F and with the second picking of orchard V, at 16.7, 16.5, and 15.8 pounds, respectively—the three pickings most nearly comparable in maturity as measured by the pressure test—a difference will be noted of 0.85 cc of sodium thiosulphate in oxidase activity for each 0.1 pound difference in pressure between orchards B and F, 0.64 cc between orchards F and V, and 0.69 cc between orchards B and V. These values appear to be significantly higher than a corresponding difference in pressure would indicate in the individual orchards, where a maximum difference of 0.38 cc is noted for a similar drop in pressure. It thus appears that orchard differences would probably militate against setting an arbitrary oxidase figure for maturity (fig. 1, B). Seasonal conditions may also be a factor.

**EFFECT OF STORAGE ON ENZYME ACTIVITY**

Bartlett pears from three orchards, harvested at three stages of maturity from each, were stored at 32° F. immediately after harvest. In table 1 are given the results of oxidase and catalase determinations at harvest and at intervals during storage. One lot, the first picking of orchard V, fluctuated irregularly throughout the storage period. This irregularity may have been due to spray materials on the fruit at harvest. With this exception, the oxidase and catalase activity were usually greater after storage than at harvest.
The effect of immaturity of fruit at harvest on its oxidase activity was magnified by holding the fruit in cold storage. This is shown graphically in figure 3, in which B (above) and V (below) represent fruit grown at elevations of about 2,400 and 850 feet, respectively. Fruit from orchard B was less mature than that picked on the same date from orchard V, and the oxidase increased more in storage. Also, the less mature fruit from orchard B showed a greater increase than the more mature fruit from the same orchard. It is significant that fruit harvested with a pressure test of 17 to 15 pounds (the pressure previously recommended for harvesting pears for canning), or below, showed comparatively little increase in oxidase activity during storage at 32° F. The greater oxidase activity in the early-picked fruit, especially after cold storage, accounts for the darker color observed in immature fruit when canned, and gives a basis for recommendations against holding immature Bartlett pears for long periods before canning. Catalase activity during storage was less closely associated with maturity at harvest than was oxidase activity.

TABLE 1.—Oxidase and catalase activity of Bartlett pears as influenced by maturity and storage

<table>
<thead>
<tr>
<th>Orchard</th>
<th>Pressure test</th>
<th>Oxidase activity after indicated number of days at 32° F.</th>
<th>Catalase activity after indicated number of days at 32° F.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pounds</td>
<td>Cr 32 57 86 135 189</td>
<td>Cr 32 57 86 135 189</td>
</tr>
<tr>
<td>B</td>
<td>20.3</td>
<td>32.8 83.5 109.0 109.0 141.0</td>
<td>13.5 19.5 26.8 33.6 44.4 31.1</td>
</tr>
<tr>
<td></td>
<td>19.3</td>
<td>21.8 50.5 47.0 50.0 57.0 45.5</td>
<td>10.6 22.0 25.6 24.4 32.6 23.9</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>19.1 18.5 26.5</td>
<td>17.4 23.6 28.7</td>
</tr>
<tr>
<td>V</td>
<td>18.4</td>
<td>23.7 14.2 28.0 16.5 24.5 10.0</td>
<td>14.3 16.8 17.3 24.2 13.9 27.1</td>
</tr>
<tr>
<td></td>
<td>15.8</td>
<td>13.0 18.5 20.0 18.5 22.5 10.3</td>
<td>10.3 16.3 20.2 21.0 26.0 19.4</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>7.9 13.0 11.5</td>
<td>17.1 27.6 33.0</td>
</tr>
<tr>
<td>F</td>
<td>16.5</td>
<td>17.4 29.0 33.5 31.5 46.0 57.0</td>
<td>4.7 9.1 12.0 15.2 23.3 13.3</td>
</tr>
<tr>
<td></td>
<td>14.7</td>
<td>11.8 17.5 15.0 18.0 25.0 20.0</td>
<td>6.3 10.0 11.0 14.5 16.8 9.1</td>
</tr>
<tr>
<td></td>
<td>13.6</td>
<td>9.5 25.5 14.5</td>
<td>11.0 14.2 19.6</td>
</tr>
</tbody>
</table>

1 Pounds pressure at harvest.
2 N/100 sodium thiosulphate per 10 cc of juice.
3 Oxygen liberated in 5 minutes by 1 cc of juice.

ENZYME ACTIVITY DURING THE GROWING SEASON

In 1938 the maturity studies were expanded to include a wider range of maturity and were limited to one orchard. Pear fruits were...
harvested from the tree in orchard V that was used in 1935. Fruit for enzyme studies was picked June 11 and at intervals thereafter until September 9, when the pressure test was 11.6 pounds. During this time the average weight per fruit increased from 19.1 g to 270.5 g. The oxidase activity of the very immature fruit was so great that it became necessary to reduce the amount of juice to 1 cc for each determination. Otherwise the procedure was the same as in the preceding year. Samples for enzyme determinations were taken immediately after the fruit was harvested.

Table 2.—Oxidase and catalase activity and rate of growth of Bartlett pears during the growing season in 1936

<table>
<thead>
<tr>
<th>Date sampled</th>
<th>Weight per fruit</th>
<th>Pressure test</th>
<th>Oxidase (N/100 sodium thiosulfate per 1 cc of juice)</th>
<th>Catalase (O₂ liberated in 5 minutes per 1 cc of juice)</th>
<th>Date sampled</th>
<th>Weight per fruit</th>
<th>Pressure test</th>
<th>Oxidase (N/100 sodium thiosulfate per 1 cc of juice)</th>
<th>Catalase (O₂ liberated in 5 minutes per 1 cc of juice)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 11</td>
<td>19.1 g</td>
<td>24.0 Cc</td>
<td>24.0 Cc</td>
<td></td>
<td>Aug. 14</td>
<td>173.8 g</td>
<td>17.9</td>
<td>3.2 Cc</td>
<td>9.0 Cc</td>
</tr>
<tr>
<td>June 24</td>
<td>33.7 g</td>
<td>13.6 Cc</td>
<td>17.4 Cc</td>
<td></td>
<td>Aug. 27</td>
<td>230.6 g</td>
<td>15.4</td>
<td>2.5 Cc</td>
<td>12.0 Cc</td>
</tr>
<tr>
<td>July 21</td>
<td>63.5 g</td>
<td>6.2 Cc</td>
<td>9.8 Cc</td>
<td></td>
<td>Sept. 9</td>
<td>270.5 g</td>
<td>11.6</td>
<td>1.5 Cc</td>
<td>21.0 Cc</td>
</tr>
<tr>
<td>Aug. 4</td>
<td>151.0 g</td>
<td>4.2 Cc</td>
<td>9.9 Cc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The effect of maturity on enzyme activity is shown in table 2 and figure 4. Oxidase activity declined very rapidly during the early part of the season and decreased more slowly as the fruit approached maturity. Catalase activity decreased until a pressure test of 17.9 pounds was reached, and then increased until the activity at the close of the experiment approximated that of the first sampling.

In the discussion of orchard location and enzyme activity it was pointed out that orchard differences would probably mitigate against setting an arbitrary oxidase figure as an index of maturity. In this connection it is of interest to compare the oxidase activity of the fruit from orchard V for the 2 years. Fruit taken from the same tree during 1935 and 1936, at pressure tests of 15.8 and 15.4 pounds, gave oxidase readings of 12.9 cc and 11.0 cc, respectively. The fruit was picked on August 26 in 1935 and on August 27 in 1936. The oxidase readings and the pressure tests indicate that the two seasons were fairly comparable. However, if the length of time from full bloom to harvest is taken as the index of maturity, the 1936 fruit, which was picked 122 days after full bloom, should have remained on the tree.
6 days longer in order to reach the 128 days allowed the fruit in 1935. The oxidase activity would then have been less, and the difference in activity between the 2 years greater. While the difference in oxidase activity between the 2 years as given above may not be particularly significant, it appears unlikely that seasonal, orchard, and growing conditions will permit arbitrary oxidase limits to be set that will be applicable as a general index of the maturity at which Bartlett pears should be harvested.

The catalase activity on August 26, 1935, and August 27, 1936, was 10.3 cc and 12.0 cc, respectively. The former was the lowest reading recorded for the year 1935. Since samples were taken 12 days before and 17 days after the August 26 sampling, it may not be the absolute minimum for the year. In 1936 a minimum of 9.0 cc was recorded on August 14, and at time of sampling, on the 27th, the activity was increasing.

**DISCUSSION**

The decrease in oxidase activity in Bartlett pears as the fruit approached maturity is in agreement with the observed behavior of pears used for canning. Previously it was reported (3) that immature pears when canned gave a product grading toward a pale orange yellow in contrast to the clear cream yellow of more mature fruit. When the immature fruit was held in cold storage for long periods before ripening, the undesirable color increased. Practices that gave a dark, undesirable color in the canned product also gave increased oxidase activity, and practices that reduced darkening reduced oxidase activity. Where initial activity was low, it remained so during storage; but if the activity was high at the beginning of storage, it increased later so that differences in maturity were exaggerated by cold storage. The decrease in oxidase activity as the fruit approached maturity is in accord with the finding of Ajon (1) with citrus fruits, of De Villiers (2) with grapes, and of Hinton (10) with apples.

Catalase activity also was high in immature pears and decreased as the fruit approached harvest maturity. However, if the fruit was permitted to remain on the tree past the commercial harvest season catalase activity increased until the fruit was tree ripe, at which time the activity approximated that observed earlier in the season. Fruit picked at intervals representing early, medium, and late commercial maturity gave lower catalase activity at the second picking. These results were duplicated in different orchards and in different years, definitely indicating that the normal catalase curve of growing pear fruits is a U-shaped curve and that if the period of sampling were lengthened the extremities of the curve would presumably be extended.

The point of minimum activity of catalase varied in intensity and in relation to pressure test. This may be seen in figure 2, in which is shown the minimum for different orchards. Orchards B and V approached nearly the same minimum but reached it at different pressure tests. In orchard F the minimum was much lower. The minimum activity recorded for orchard V for the 2 years was 10.3 cc and 9.0 cc, respectively. If samples had been taken at shorter intervals a closer agreement between the minimum activity for the 2 years might possibly have been recorded.

While catalase activity does not appear to be correlated with color in the canned product it may be indirectly related to quality, since
the low point in the catalase curve occurs near the stage at which the fruit should be picked for canning in order to secure best results.

The low point in the catalase curve may also indicate a critical stage in the metabolism of the fruit, since it coincides with the period of minimum respiratory intensity (4) and also with the pressure test usually recommended in the Wenatchee district for the harvesting of Bartlett pears for best dessert and storage quality.

These results with pears lead the writers to suspect that the catalase curve of apples may also be a U-shaped curve and that the low results reported by Hinton (10) in his middle picking of apples may have been due to this characteristic of the catalase activity rather than to the cold weather to which he ascribed his results.

That the low points in the catalase curves in the present work are not due to low temperatures just before harvest may be seen from an examination of figure 2, which shows that fruit from different orchards, exposed to similar temperatures, reached the minimum in catalase activity at different times. Furthermore, in figure 4 the mean temperatures for the 7 weeks preceding harvest were 62°, 69°, 75°, 76°, 76°, 66°, and 70° F., respectively. Any correlation that might be found in this case between temperature and catalase activity of the fruit while still on the tree would evidently be a negative one.

It is not particularly surprising that the catalase curve should be U-shaped. Overholser (14) reported that immature Bartlett pears were high in catalase, which decreased as maturity advanced. His results indicated a continuous decrease. However, a study of his data permits some interesting comparisons to be made. Since it is not known how mature his fruits were at the time of final sampling, it may be possible that he discontinued sampling before the rise in catalase began. This hypothesis is supported by the fact that on May 28 the average weight of his pears was 15.2 g; on June 11 the average weight of the authors' pears was 19.1 g. Assuming that the rate of growth before the first sampling was approximately equal in the two cases, then the season of his study was about 2 weeks earlier than the season in which this study was made. If this is true, he discontinued sampling approximately 110 days after full bloom. The minimum activity recorded in the present study was 109 days after full bloom. If the number of days from full bloom be taken as the measure of maturity, he discontinued sampling at the stage of maturity at which the least activity was found in the work covered by this paper, and his results might be said to agree with those presented here. His report of 8.6 cc and 8.4 cc of oxygen liberated on July 27 and August 4, respectively, would indicate the low points in the catalase curve had been reached. Overholser mentioned that his results did not agree with Reed's findings of increase of catalase activity with ripening in the case of pineapples, when green, hard yellow, and fully ripe fruits were used.

When Bartlett pears are permitted to remain on the tree until tree-ripe, there is a tendency for the flesh to break down at the core. Harding (8) and Neller (12) have reported increased catalase activity of apples in storage as they approach the break-down stage. It is possible that the accumulation of acetaldehyde and alcohol which takes place as fruit approaches the break-down stage stimulates catalase production, causing the rise in activity. This viewpoint is strengthened by the increase in catalase activity of fruit subjected to alcohol vapors (4).
SUMMARY

The effect of maturity and handling practices on the oxidase and catalase activity of Bartlett pears has been studied in relation to the observed behavior of pears used for canning.

Oxidase activity decreased throughout the growing season.

The catalase activity of Bartlett pears from the time they were very small until they were tree-ripe formed a U-shaped curve. The minimum activity occurred near the period at which the fruit should be harvested for canning.

High oxidase activity is correlated with practices that give an undesirable color in canned pears, and low oxidase activity is correlated with practices that give a desirable color. It therefore appears that high oxidase activity may be the principal cause of poor color in the canned product.

Catalase activity apparently is unrelated to color development in canned Bartlett pears but may be related indirectly to quality since best results are obtained with fruit picked when the low point in the catalase curve is reached or soon thereafter.

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