

The Effect of Bruising and Aging on the Texture and Pectic Constituents of Canned Red Tart Cherries^a

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SUMMARY

Red, tart cherries allowed to stand before being canned, either with or without having been previously bruised, were much firmer after canning than were similar cherries canned immediately after harvest. During the aging period a portion of the pectin was completely demethylated to form pectic acid. Most of the pectin, however, was apparently unchanged in chain length or degree of esterification. Histological examination of the tissue showed that the cell walls of the aged cherries were more rigid and less easily separated from each other than were the cell walls of cherries canned immediately after harvest.

INTRODUCTION

Red, tart cherries are harvested during midsummer when the temperature is often 80–90°F. The cherries are severely bruised in commercial harvesting (Whittenberger, 1952). The period between harvest and unloading at the plant may be 4, 8, or even 20 hr. This constitutes an aging period, unintentional but nonetheless important. In addition, at the processing plant, the cherries are commonly soaked in cold water for 6–20 hr to chill, clean, and firm them before pitting. Thus there are two aging periods, one in air and one in water.

Whittenberger and Hills (1953) reported that aging in air or in water at various temperatures increased yield (weight of cooked, drained cherries/weight of fresh, whole cherries) and gave a firmer texture. If the cherries are bruised before the aging period, the increase in yield may be even more pronounced. The aged or bruised and aged cherries are firmer, have a greater bulk volume, and retain their rounded shape better than do unaged cherries. This is shown in Fig. 1. Fig. 2 shows the shapes of a few individual cherries from each container.

The water-insoluble constituents of tart cherries are being investigated with a view to determining whether they are changed by bruising and aging before canning. This paper reports the effect of these treatments on the pectic compounds and on the appearance of the cell walls.

METHODS

Chemical investigations. Preparation of samples. Montmorency cherries from orchards in Michigan, Pennsylvania, and New York State were used. The cherries were picked carefully by

hand, put immediately into ice water, and taken to the processing plant. The control cherries were drained, weighed, and canned immediately. Cherries for the aging treatment were drained, weighed, and allowed to stand at room temperature for 24–48 hr before being pitted. Bruising was done by dropping the cherries several times, a few at a time, onto an inclined tray from a height of 1–3 ft. The bruised cherries were then either canned at once or aged first.

Cherries in all treatments were pitted, exhausted to a center can temperature of 170°F, sealed, and cooked 12 min in a boiling water bath. Analyses were made several months after canning and were calculated on the basis of fresh whole fruit.

The canned cherries were ground in a Waring blender, mixed with 3½ volumes of ethyl alcohol, allowed to stand overnight, and then filtered through a nylon cloth. The alcohol-insoluble solids were dried and used for pectin and pectic acid extractions.

Pectin. Water was added to the dry alcohol-insoluble solids in a tared beaker to form a slurry, which was then adjusted to pH 1.8 with hydrochloric acid and heated 1 hr on a steam bath. After heating, the weighed slurry was filtered through a nylon cloth and the filtrate weighed. Pectin was precipitated from the filtrate with acidic ethyl alcohol, washed, dried, and weighed, correcting for the amount held in the unfiltered solids during the filtration (Owens *et al.*, 1952). The insoluble solids on the filter cloth were rinsed with hot water, returned to the beaker, and twice re-extracted at pH 1.8 on the steam bath, for ½ hr each time. After the last extraction, the non-pectin insoluble solids were thoroughly rinsed with hot water, alcohol, and acetone, dried, and saved for pectic acid extraction.

Pectic acid or polygalacturonic acid. Water was added to the insoluble solids from which pectin had been extracted, and small amounts of dilute sodium hydroxide were added over a period of several hours with intermittent stirring, care being taken that pH never rose above 7.5. When the pH had remained at 7.5 for 2 hr without dropping, the solution was filtered and the solids re-extracted twice more in the same way. The filtrate was acidified with hydrochloric acid, three volumes of alcohol were added, and the precipitated pectic acid was filtered off, washed, dried and weighed.

Esterification. Percent esterification was determined by the method described by Owens *et al.* (1952). For the pectic acid precipitate, the method of Feldstein and Klendshoj (1954) for methanol was also used.

Anhydrouronic acid. Anhydrouronic acid was determined by the method of Ikawa and Niemann (1949).

Calcium. The procedure of Appleton *et al.* (1959) was followed, with calcein used as the indicator. However, when pectic acid or other insoluble samples were analyzed, the method was modified by extracting with ethylenediaminetetraacetic acid (EDTA) and back-titrating with standard calcium solution.

Histological investigations. The cherries used were obtained from an orchard at Biglerville, Pennsylvania. They were picked and hauled in cold water to the processing plant, as were the samples for chemical analysis. The control cherries were canned immediately by the usual procedure, but without being pitted. Those given the aging treatment were allowed to stand 48 hr at room temperature, and then canned, also without being pitted.

The canned cherries were fixed in formalin-acetic acid-alcohol solution, and then washed in water until free of alcohol.

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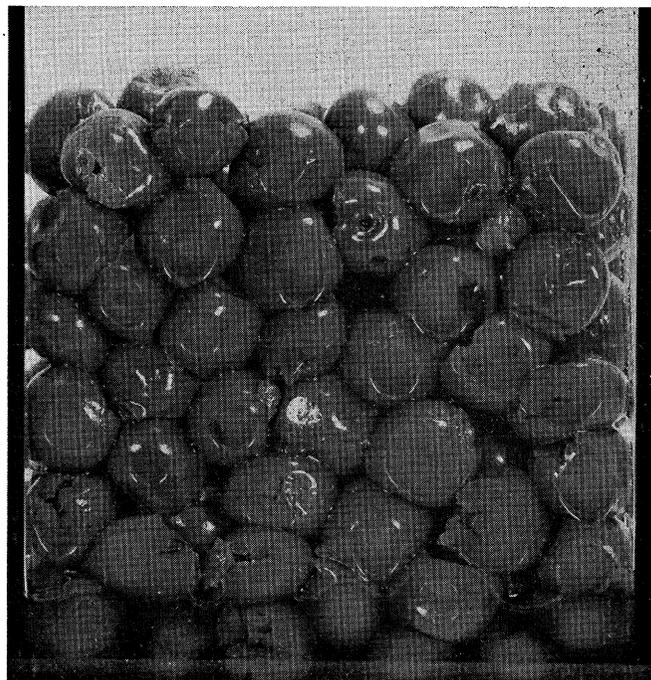


Fig. 1. Effect of bruising and aging on firmness of red, tart, pitted cherries. Each jar contains pitted, canned cherries equivalent to 450 g of fresh, whole cherries. Left, control, processed immediately after harvesting. Drained weight = 68%. Right, cherries bruised twice by dropping from a 2-ft height, allowed to stand 8 hr in air at room temperature, and then 16 hr in ice water before being processed. Drained weight = 74%.

After they had been quartered and the pits removed, radial sections of 240 or 300 μ were cut on a freezing microtome. Those sections which were not to be extracted were stained with ruthenium red or methyl green and mounted in glycerine jelly. The rest of the sections were transferred to 0.5N hydrochloric acid and heated 2 hr on a steam bath to extract the pectin. After being washed, some of the sections were stained and mounted in the same way as the untreated sections. The remaining sections were placed overnight in buffer at pH 7.5 to remove the pectic acid. After being washed, the sections were stained and mounted in the usual way.

RESULTS

Chemical investigations. Table 1 shows mean values from analyses of samples from Michigan for one season. Results were similar for other seasons and other areas, but the exact values varied from location to location and season to season. In addition, severity of bruising and time and temperature of aging varied for the individual locations and seasons, since it was desired to get the maximum firming effect without mangling the fruit or allowing it to spoil. Samples in Table 1 are arranged in order of increasing severity of treatment. Sample B, although supposedly given no aging period, was actually aged for 20–30 min after bruising, since it took about that long for the cherries to be pitted and heated to boiling. This was not long enough to firm the cherries visibly, and the bruising may even have softened them somewhat by mechanically rupturing the cells, but apparently it was long enough for some enzymatic change to take place. Sample C was much firmer than A and B, and sample D was slightly firmer than C. In the case of D, the time elapsed after bruising was enough that the cherries recovered from the mechanical effects of the bruising and be-

came even firmer than C, which was aged for the same period but not bruised before being aged.

The amount of the pectin precipitate decreased with increasing severity of treatment. Since the pectin precipitate was fairly impure, containing only about 60% anhydrouronic acid (AUA), a better measure of the acid-soluble pectin content is given by calculating it on the basis of the percent AUA found in the pectin precipitate. The control was found to contain 0.16% pectin as AUA, and the most severe treatment, bruised and aged, 0.10%, almost a 40% reduction. The chain length of the pectin, as measured by viscosity of the pectin solution, did not appear to differ among the treatments. The degree of esterification, usually 45–55%, tended to be somewhat variable, but did not decrease much, if at all, with treatment.

Pectic acid, as shown in Table 1, increased in the treated samples. In the case of the most severe treatment, bruised and aged, the increase was about threefold. The amount of alkali necessary to neutralize and extract the pectic acid from the acid-insoluble solids increased from sample A to D. This was proportional to the amount of pectic acid present. The isolated pectic acid had an AUA content of about 80% and an equivalent weight by titration of 195, compared to the theoretical value of 176 for anhydrogalacturonic acid.

The carboxyl groups of pectic acid were esterified only about 2% as determined both by the titration method (Owens *et al.* 1952) and by the more specific methyl determination of Feldstein and Klendshoj (1954). No relation was found between firmness and the calcium content of the pectic acid, or with the calcium content of the pectin or remaining insolubles.

Although no derivatives were made, the pectic acid hydrolysate resembled galacturonic acid in its paper chromatographic characteristics and in its ultraviolet absorption spectrum after reaction with 79% sulfuric acid (Ikawa and Niemann, 1949). Furthermore, when borate was added in the latter reaction, there was no shift in the wavelength of maximum absorption, as would have been the case if glucuronic rather than galacturonic acid had been present (Gregory, 1960).

The weight of insoluble solids remaining after removal of pectin and pectic acid was higher in the firm than in the soft cherries. The component responsible for this difference is still being investigated. (Plates follow; text continued p. 530)

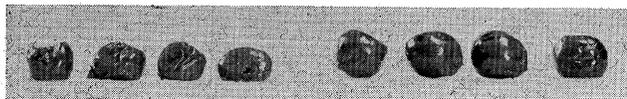
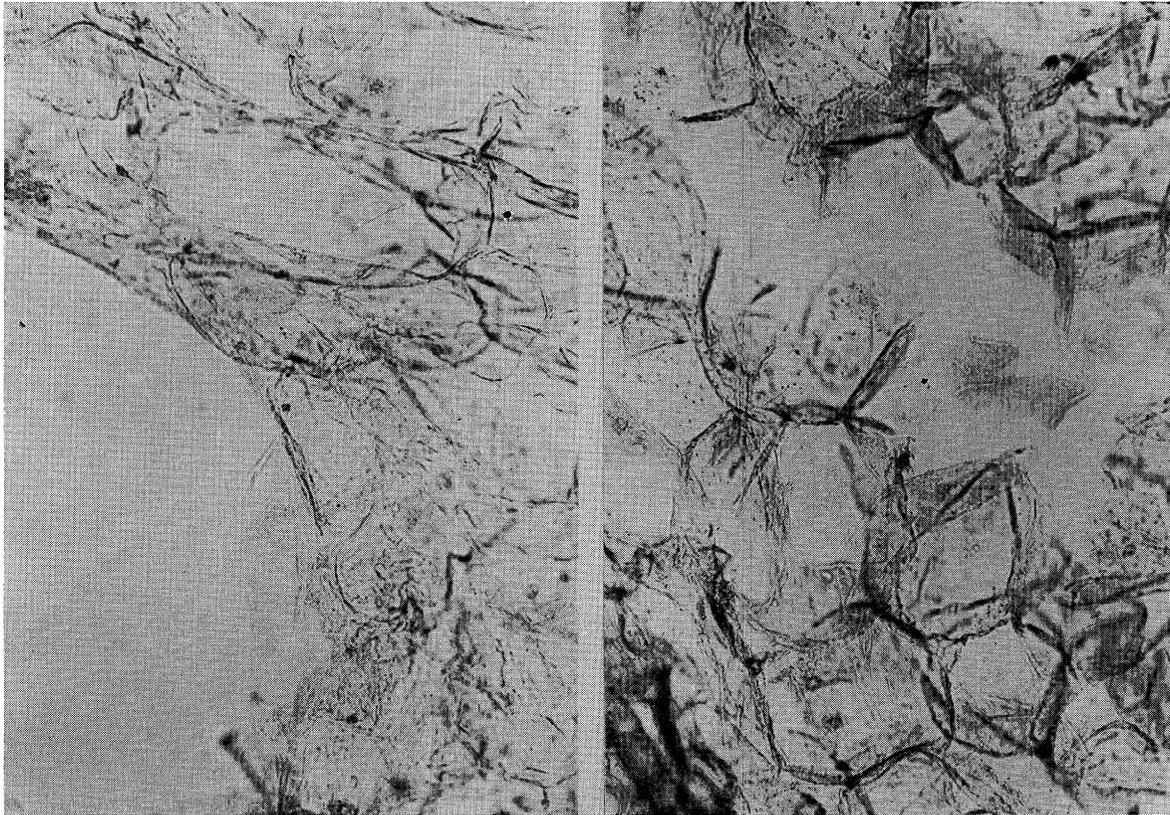


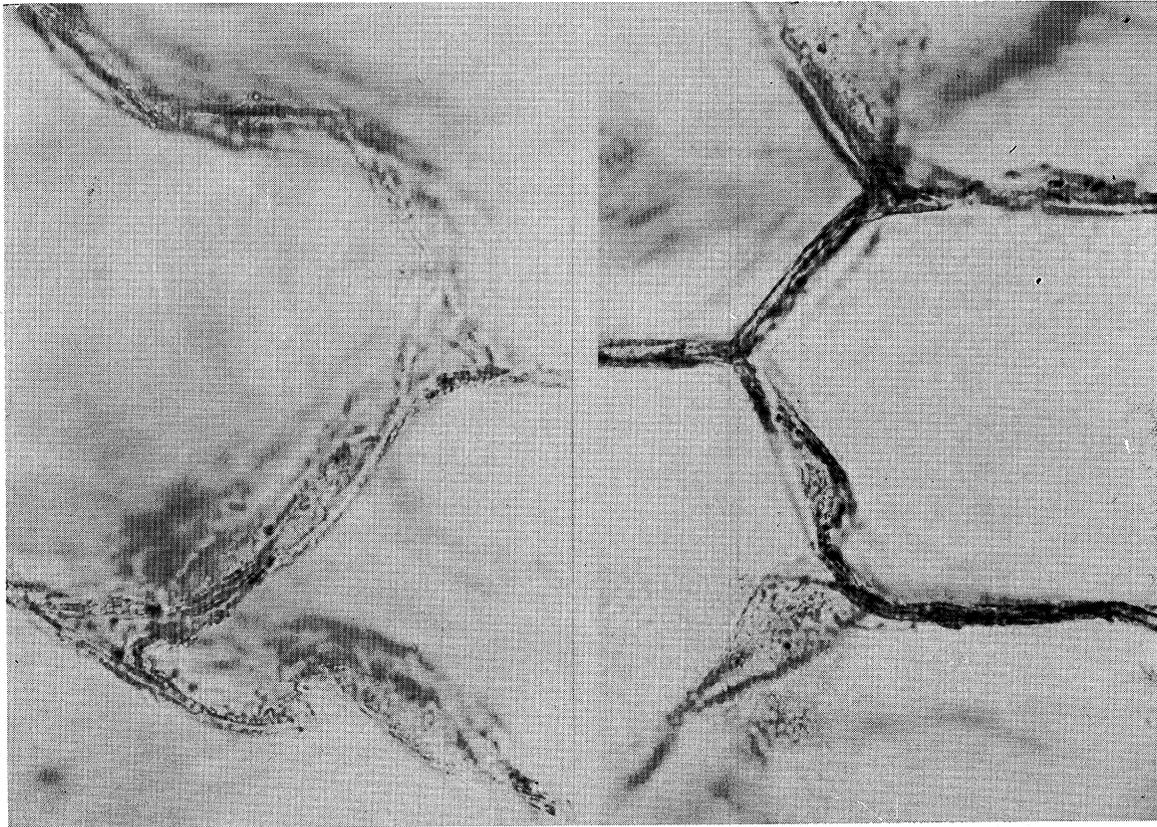
Fig. 2. Effect of bruising and aging on appearance of individual cherries. Cherries on left and right received the same treatments as those in Fig. 1.



CONTROL

A

FIRMED

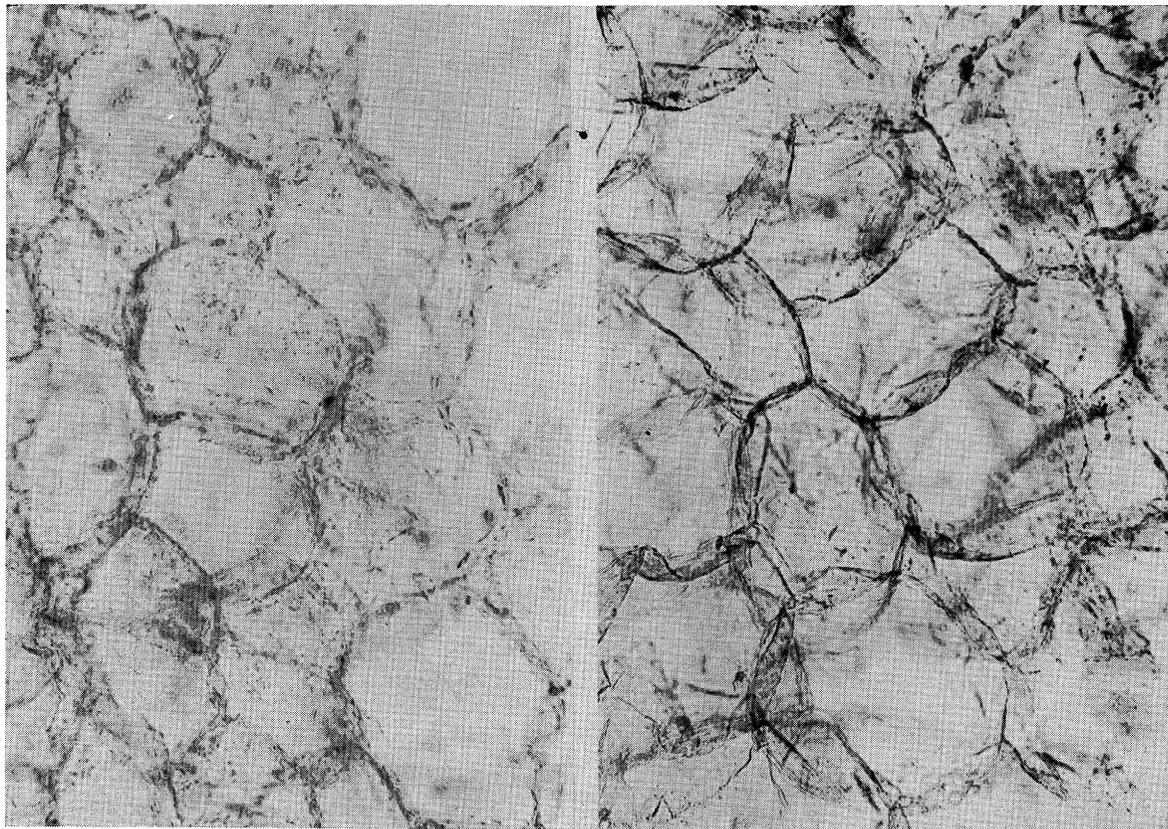


CONTROL

B

FIRMED

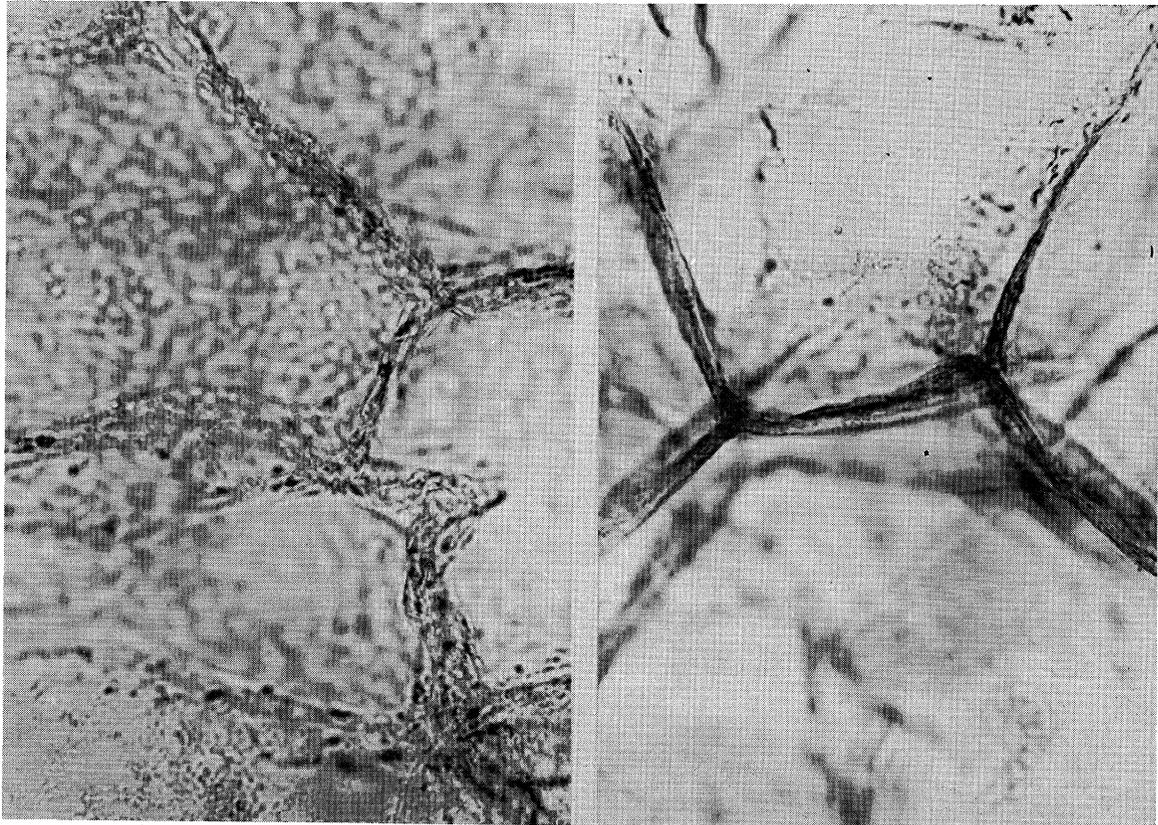
Fig. 3. Photomicrographs of radial sections of red tart cherries, stained with methyl green. Control was canned immediately after harvesting. Firmed was allowed to stand 24 hr at room temperature before being canned. A) $\times 125$; B) $\times 500$.



CONTROL

A

FIRMED



CONTROL

B

FIRMED

Fig. 4. Photomicrographs of radial sections of red, tart cherries after extraction of pectin with acid, stained with methyl green. Control was canned immediately after harvesting. Firmed was allowed to stand 24 hr at room temperature before being canned. A) $\times 125$; B) $\times 500$.

Table 1. Results of analyses of red, tart, pitted cherries firmed by bruising and aging before canning.

| Sample no. | Treatment | Percentage of raw, unpitted fruit | | | | | |
|------------|---------------------------------------|-----------------------------------|---|---------------------------|--|-----------|----------------------------|
| | | Pectin (gravimetric) | Pectin (calculated on basis of AUA content) | Pectic acid (gravimetric) | Pectic acid (calculated on basis of AUA content) | Total AUA | Insoluble solids remaining |
| A | Control, not aged or bruised | 0.27 | 0.16 | 0.04 | 0.03 | 0.19 | 0.34 |
| B | Bruised 3 times from 3 ft, not aged | 0.23 | 0.14 | 0.06 | 0.05 | 0.19 | 0.35 |
| C | Aged 24 hr, not bruised | 0.18 | 0.11 | 0.10 | 0.08 | 0.19 | 0.37 |
| D | Bruised 3 times from 3 ft, aged 24 hr | 0.17 | 0.10 | 0.12 | 0.10 | 0.20 | 0.39 |

Histological investigations. Fig. 3-A shows cell walls of untreated and of firmed, canned cherries. When the section was gently pulled apart with a pair of needles, adjacent cell walls in the soft or untreated cherries separated easily, the cells remaining whole. When, however, the tissues of aged, firm cherries were pulled apart, the cell walls tended to fracture rather than separate at the middle lamella, leaving sharp edges of broken cell walls. Furthermore the control sections were easily pulled out of shape whereas sections from the firmed cherries were very rigid and resisted distortion.

Fig. 3-B shows the same sections at a higher magnification. As can be seen, there was not much difference in the cell walls themselves. Both methyl green and ruthenium red appeared to stain the whole cell wall indiscriminately, indicating either that the stains were not specific for cellulose and pectic substances, respectively, or that the cell walls were composed of a complex of associated polysaccharides that could not be resolved at this magnification. No difference in degree of esterification was found among treatments with the hydroxylamine test of Gee *et al.* (1959), with visual comparison.

Fig. 4 shows the appearance of the sections after the pectin had been extracted with hot hydrochloric acid. The firmed cherries still had definite cell walls, whereas in the soft cherries the cell walls had almost lost their identity. When the pectic acid remaining in the sections was extracted with dilute sodium hydroxide, the cell walls of the soft cherries lost what little cell wall structure they had left, whereas the firmed cherry sections were apparently unchanged.

When sections were treated with pectin methylesterase and polygalacturonase instead of the chemical treatments to remove pectin and pectic acid, the cell walls of the control cherries disintegrated but the cell walls of the firmed cherries remained unchanged.

Cell walls of control and firmed cherries differed less when sections were made from raw cherries than when canned cherries were used. However, when pectin was extracted from the sections, cell walls of the raw cherries looked like those of extracted canned cherries, as in Fig. 4.

DISCUSSION

When cherries are allowed to stand before being pitted, they are, of course, still alive and respiring. Bruising increases the respiration rate of cherries (Pollack *et al.*, 1958), just as it does with other plant tissues. Something apparently occurs between harvesting and canning that increases the rigidity of the cell walls, so that the cherries maintain their rounded shape, have a greater bulk volume, and appear to hold more water and hence weigh more than do cherries canned immediately after harvest.

In studies of the tissue softening of fruits during ripening, textural changes have been found to be related to changes in the percent esterification of the pectin in the cell walls or the middle lamella. Van Buren *et al.* (1960) reported that snap beans become firmer during the blanching period because of demethylation of the pectin by pectin methylesterase to the less soluble pectic acid. Toughening of stored frozen cherries was also found to be related to a lower

degree of esterification of the pectin (Gee and McCready, 1957). In the firming of aged and bruised-aged cherries, however, the degree of esterification of most of the pectin is changed very little if at all. At the same time, another portion of the pectin, perhaps that located in the middle lamella or in some specific part of the cell wall, is almost completely demethylated. This demethylation occurs while the cherry is still alive and may quite possibly be due to increased pectin methylesterase activity.

The canning process, in which cherries with a pH of about 3.5 are heated, may also be looked upon as a mild pectin extraction. Pectin, therefore, is partially removed during canning. This may account for the fact that histological differences between control and treated cherries were greater in canned than in raw fruit. With some of the pectin removed, the control cherries are flabby and easily distorted, and the non-rigid cell walls readily separate from each other. The extreme, of course, is the complete removal of pectin by heating with acid or treatment with pectin enzymes, which causes near disintegration of the sections. The treated (firm) cherries, in contrast, have a definite, rigid cell wall structure even when the pectin is removed. The presence of pectic acid may contribute to this increased cell wall rigidity, but since the rigidity is maintained even when all pectic acid is removed with sodium hydroxide, it seems likely that still another factor is involved. At any rate, during the aging period some compound is formed that imparts sufficient rigidity to the cell walls that the cooked cherry is still firm and resists distortion.

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