

Effect of Calcium Chloride on
Firmness of Some Canned
Products and on Their
Content of Ascorbic Acid

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Most berries and such vegetables as asparagus and spinach undergo considerable breakdown of tissues upon being canned. Since the grade of canned foods depends to some extent on their wholeness and firmness, it is desirable to find a method by which such qualities can be preserved. Addition of a small amount of calcium chloride to tomatoes for canning has proved successful in firming the tomatoes (Kertesz *et al*, 1939 and 1940; Godfrey, 1940; and Laconti 1941 and its use in canning has been made permissible by an amendment of the Federal Food, Drug, and Cosmetic Act (1940)¹. To find whether calcium salts may have a similar effect on other soft foods, tests were made in the present studies on red raspberries, strawberries, gooseberries, rhubarb, plums, and asparagus. Four pints of each were canned without the addition of calcium and three lots of four pints each were canned adding calcium chloride to give concentrations of 0.05, 0.07, and 0.09 percent. The following year, tests were repeated on red raspberries, using two different varieties, Latham and Cuthbert. The asparagus and plums were purchased on the open market. The rhubarb and one lot of raspberries were obtained from a local grower. All the rest of the berries were picked on the Experiment Station farm at Lexington.

METHODS

All the products were canned in pint glass jars and processed in the oven at 275° F. Asparagus was washed and cut into $\frac{3}{4}$ -inch pieces. Rhubarb was washed, peeled, and cut into $\frac{3}{4}$ -inch pieces. Plums (Italian Prunes) were washed and each one pricked 24 times to prevent the skin from breaking. Gooseberries were washed and stemmed. Strawberries were washed and the calyxes removed. Raspberries were washed. The following proportions were the amounts used per pint jar: asparagus 300 g, water 300 g, processed 3 hours; rhubarb 500 g, sugar 135 g, rhubarb juice 40 g, processed 30 minutes; plums 350 g, sugar 30 g, water 110 g, processed 50 minutes; gooseberries 275 g, sugar 100 g, processed 50 minutes; strawberries 500 g, sugar 200 g, processed 30 minutes.

¹ Use of calcium salts other than calcium chloride, has been made permissible since these studies began, by further amendment. — (Secs. 401, 701, 52 Stat. 1046, 1055; 21 U.S.C. 341, 371).

Raspberries were canned with and without sugar and with and without water. Three hundred grams of raspberries were used, 70 g sugar when sugar was used, and 155 g water when water was used, processed 30 minutes.

The calcium chloride at concentrations of 0.05, 0.07, and 0.09 percent of the contents of the jar was thoroughly mixed with either the sugar or the water, which was then added to the food and carefully mixed to get uniform distribution.

The jars were all stored in a cool, dark place. One lot of each product was opened after 4½ to 6½ months, and a second lot after 13 to 16½ months.

It is important that any treatment used for firming tissue have no adverse effect on flavor, keeping quality, or nutritive value. Scoring for the value of the calcium treatment was based, therefore, on evidence of satisfactory flavor, ascorbic acid content, and drained weight. Ascorbic acid was chosen as the criterion for nutritive value because it is probably the least stable of the nutritive factors of foods and would therefore probably be affected most by treatment of the food. In addition, it seemed desirable to know the ascorbic acid values because fruits and vegetables are valuable sources of that vitamin. Drained weight has been quite generally accepted as the criterion for measuring intactness of tissue (1941), since there is a direct relationship between drained weight and firmness. A committee of five persons, experienced in scoring foods, judged flavor and texture. No bacterial tests were made, inasmuch as the canning had been done according to approved procedures.

Both dehydro and l-ascorbic acid were determined by the method of Emmerie (1934) with modifications according to Kolesnik (1938) on aliquot portions of the contents of each jar. A corresponding aliquot portion of the juice was always included with each portion of asparagus or fruit tested. Size of sample and dilution with water were dependent on the ascorbic acid content. The sample was acidulated with concentrated acetic acid so that there was an equivalent concentration of 5 percent acetic acid. The acidified mixture was mixed thoroughly and filtered, and filtrate decolorized by shaking for 2 minutes with 2 grams of calcium carbonate and 2 grams of lead acetate and filtered. Excess lead was removed by treatment with hydrogen sulfide for 10 minutes. The mixture was then filtered and carbon dioxide run in until there was no trace of hydrogen sulfide. An aliquot of the clear, colorless filtrate was titrated with dilute sodium 2,6-dichlorophenol-indophenol standardized against an ascorbic acid solution.

Drained weight was measured by the method described by the Bureau of Agricultural Economics of the U. S. Department of Agriculture (1941). Eight-mesh sieves were used, the wire diameter of which was 0.028 inch and the openings 0.097 inch.

RESULTS

Flavor and Texture

Combined scores of the judges indicated that calcium chloride in the three concentrations did not affect the flavor of raspberries, gooseberries, or asparagus nor did it affect the flavor of strawberries, plums, or rhubarb until the concentration reached 0.09 percent, at which point the judges objected to the saltiness. Texture of asparagus, gooseberries, and strawberries was not affected. Texture of plums was improved by the addition of calcium chloride at all three concentrations. Rhubarb texture was judged best at the 0.07-percent level and less good but not poor at the 0.05-percent and 0.09-percent levels. Texture of raspberries, both those canned with water and those canned without water, was scored slightly better with each increase in calcium percentage. Improvement in texture of plums and rhubarb, and of raspberries canned without water, noted by the judging committee, did not agree with the figures for drained weight, but a relationship was observed between drained weight and texture in the raspberries canned with water.

Ascorbic Acid

Plums opened at the end of three months and rhubarb opened at the end of 6½ months showed no effect of calcium chloride on ascorbic acid, but some protective effect was noted in the first lots of strawberries, raspberries, and gooseberries (Table 1). In strawberries the ascorbic acid content was highest in those canned with calcium chloride at 0.05-percent concentration. In gooseberries treated with calcium chloride at 0.09-percent concentration, but not in those with the lower percentages of the calcium salt, the ascorbic acid content was higher than that of the control. In raspberries canned without water and in asparagus the ascorbic acid content where calcium chloride was used at concentrations of 0.05 and 0.07 percent was lower than in the control, and where it was used at concentrations of 0.09-percent the ascorbic acid content was about the same as in the control. On the other hand, in raspberries canned with water, the ascorbic acid content was higher in the calcium-treated lots than in the control,

Table 1.—Ascorbic acid content and drained weight of canned fruits, rhubarb, and asparagus, without and with Calcium Chloride

Concentration of CaCl ₂	Percent drained weight		Mg percent ascorbic acid	
	Analyzed after 4.5 to 6.5 mo.	Analyzed after 13 to 16.5 mo.	Analyzed after 4.5 to 6.5 mo.	Analyzed after 13 to 16.5 mo.
Asparagus				
0	94.7 91.0	87.7 91.7	6.07	0.36
0.05 percent	93.3 89.3	87.3 90.6	4.75	0.41 0.38
0.07 percent	91.3 94.0	88.3 88.3	4.90	0.40 0.23
0.09 percent	92.3 93.7	87.0 90.3	5.83	0.44 0.39
Rhubarb				
0	78.0 70.6	75.6	3.11	0.62
0.05 percent	71.6 71.4	74.0 73.4	3.35	1.78 0.36
0.07 percent	73.0 71.0	74.6 74.4	3.41	1.59 0.83
0.09 percent	72.0 70.6	72.8 74.4	3.61	0.53 0.40
Plums				
0	84.0 78.3	80.0 77.1	0.67	0.56 0.37
0.05 percent	85.7 78.3	78.0 74.3	0.55	0.67 0.32
0.07 percent	80.0 78.3	78.9 79.1	0.75	0.40 0.26
0.09 percent	80.0 80.3	80.6 77.1	0.68	0.32 0.37
Gooseberries				
0	70.9 76.4	71.3 85.8	3.07	2.42 2.49
0.05 percent	68.0 71.6	74.2 85.1	3.60	0.92 1.82
0.07 percent	64.7 72.7	73.5 83.6	2.84	0.42 1.55
0.09 percent	72.7 73.8	74.2 80.7	5.57	0.40 0.54
Strawberries				
0	52.8 55.0	55.2 55.4	9.20	3.89 7.20
0.05 percent	57.2 54.6	80.0 56.2	14.21	6.51 7.07
0.07 percent	54.8 56.6	55.8	8.87	8.82
0.09 percent	56.0 53.8	56.4 54.4	9.23	4.01 4.50
Raspberries with sugar, without water (Latham, good quality)				
0	83.3 82.7	81.7 82.7	3.31	0.061 0.197
0.05 percent	82.0 85.3	80.3 81.7	1.56	0.124 0.114
0.07 percent	83.3 80.7	84.3 83.0	1.56	0.200 0.171
0.09 percent	83.0 80.7	84.3 80.0	3.08	0.171 0.072

Table 1, continued

Concentration of CaCl ₂	Percent drained weight		Mg percent ascorbic acid	
	Analyzed after 4.5 to 8.5 mo.	Analyzed after 13 to 18.5 mo.	Analyzed after 4.5 to 8.5 mo.	Analyzed after 13 to 18.5 mo.
Raspberries with sugar and water (Latham, good quality)				
0	78.0	88.7	4.17	1.41
	68.7		4.94	
	75.3			
	79.0			
0.05 percent	86.7	88.0	3.92	1.20
	83.3		3.75	
	80.0		3.45	
	72.7			
	73.0			
0.07 percent	88.0	92.0	5.00	0.33
	93.3		4.31	
	83.3		4.27	
	84.3			
	74.6			
0.09 percent	86.7	89.7	3.45	1.18
	86.3		3.63	
	85.7			
	71.7			
Latham, over ripe				
0	74.6		4.85	
	77.7		4.63	
0.05 percent	80.0		5.67	
	75.0		5.41	
0.07 percent	78.3		5.44	
	83.3		4.62	
0.09 percent	78.7		5.00	
	79.7			
Outhbert, over ripe				
0	82.3		3.98	
	76.0		2.81	
0.05 percent	69.7		4.61	
	73.3		4.35	
0.07 percent	78.3		3.79	
	78.0		4.78	
0.09 percent	78.7		5.20	
	80.0			
Raspberries without sugar, with water (Latham, good quality)				
0	70.0		4.80	
	77.3		5.30	
0.05 percent	81.0		4.19	
	86.7		3.48	
0.07 percent	81.3		4.10	
	86.7			
0.09 percent	69.7		3.63	
	65.7		4.80	
Latham, over ripe				
0	72.7		5.37	
	70.3		5.54	
0.05 percent	74.7		5.78	
	67.0		4.97	
0.07 percent	73.3		7.14	
	72.7		6.85	
0.09 percent	78.3		5.47	
	83.3		6.20	
Outhbert, over ripe				
0	75.3		3.98	
	78.7		3.33	
0.05 percent	84.0		3.89	
	80.7		4.28	
0.07 percent	79.0		3.98	
	75.0		4.22	
0.09 percent	78.3		3.44	
	81.7		5.51	

those treated with calcium chloride at 0.09 percent having about twice as much as the control.

Raspberries canned the second year of the experiment were all canned with water, half of each lot with sugar and half without sugar. Two lots of Latham berries were picked on the Experiment Station farm and one lot of Cuthberts was purchased from a local grower. One lot of Lathams and all of the Cuthberts were considered excellent for immediate eating but overripe for canning. Of both varieties, those canned with calcium chloride had more ascorbic acid than the controls (Table 1). Also, the very ripe Latham berries had considerably more ascorbic acid than the Cuthberts. The second lot of Lathams, which were firmer and better for canning, had slightly more ascorbic acid than the Cuthberts but there was very little difference between the ones canned with and those canned without calcium chloride. There was practically no difference between those canned with sugar and those canned without sugar.

Degree of ripeness in the Latham berries seemed to affect the ascorbic acid content, the riper berries having a higher ascorbic acid value. The Cuthbert berries, which were also at the peak of ripeness, had less ascorbic acid than either lot of the Lathams. This may have been a variety difference.

All of the products kept for the longer period before being opened, that is, from 13 to 16½ months, had less ascorbic acid than those analyzed after 4½ to 6½ months, nor could a protective effect of calcium chloride be noted.

In strawberries and plums kept for the longer period the ascorbic acid content averaged 37 percent less than in those kept the shorter period, in gooseberries, rhubarb, and raspberries canned with water, approximately 70 percent less, and in asparagus and raspberries canned without water about 94 percent less. The results cannot be attributed to the effect of light because the jars were stored in darkness during the 16-month period.

The validity of the procedure and technique for determining ascorbic acid by the method of Emmerie (1934) with modifications according to Kolesnik (1939) were checked by recovery tests, using 0.0024 milligrams of pure ascorbic acid and running the tests at intervals during the experimental period (Table 2).

The calcium-treated plums, gooseberries, and asparagus tested 4 to 6 months after being canned had lost about the same percentage of weight as the controls (Table 1). A slightly higher drained weight was noted in the strawberries to which calcium had been added. Of

Table 2.—Recovery Tests on Ascorbic Acid¹

Dilute sodium 2,6-dichlorophenolindophenol solution required to titrate 0.0024 mg. ascorbic acid		Percent recovery
Without decolorizing	Treatment with reagents used for decolorizing	
ml	ml	
0.075	0.070	93
0.074	0.072	97
0.074	0.072	97
0.042	0.042	100
0.052	0.050	96
0.042	0.0435	104
0.027	0.030	111
0.048	0.0445	93

those held for the longer period, there was practically no difference between the calcium-treated products and the controls, but strawberries and gooseberries held for the longer period had a greater drained weight than those held for the shorter period and asparagus had slightly less. This effect was noted in both the calcium-treated products and the controls. Rhubarb, at all three levels of calcium addition, had a slightly lower drained weight than the control after 6½ months. The effect was still apparent at the end of 14½ months, at which time all four of the rhubarb packs had higher drained weight than those tested after 6½ months. Raspberries, canned with water, were definitely firmed by the addition of the calcium salt, the best result being obtained at the 0.07-percent level of calcium chloride addition. The effect was noted both in the berries held the short period and in those held for the long period. All the raspberries held 13 to 16½ months had higher drained weight than those held 4½ to 6½ months, as was true of all the other foods except asparagus. In raspberries canned without water, there was little or no effect of the calcium salt on drained weight, neither over the short nor the long period.

The tests carried out the second year of the experiment on raspberries canned with and without sugar (Table 3), on two lots of Latham berries and one lot of Cuthberts, confirmed the results of the first year's tests — namely, that the addition of calcium chloride tends to firm the

Table 3.—Ascorbic acid content and drained weight of red raspberries canned with and without sugar¹

Concentration of CaCl ₂	NO SUGAR		WITH SUGAR	
	Percent drained weight	Percent ascorbic acid, mg.	Percent drained weight	Percent ascorbic acid, mg.
0	74.1	4.72	77.5	4.23
0.05 percent	79.0	4.43	74.0	4.61
0.07 percent	79.5	5.26	76.5	4.54
0.09 percent	76.2	4.84	76.2	4.56

¹ Raspberries canned the second year of the experiments.

tissue. The results were not entirely consistent in that, in some cases, the 0.05-percent level seemed to be most effective; in other cases the 0.07-percent level, and in one instance the 0.09-percent level seemed best. In the raspberries canned without sugar the effect of the calcium chloride on drained weight was marked, the drained weight being higher at all three levels of calcium addition. In all those to which sugar had been added, however, the drained weights of the calcium-treated samples were lower than of the control.

The theory advanced for the effect of calcium salts on the firming of tissue of canned products is that the calcium combines with the pectic materials and forms a gelatinous insoluble calcium pectate in the tissues. Otherwise there is a tendency for the pectin to go into solution and leave the body of the fruit or vegetable when it is heated with acids, sugar, or salts (Strasburger, 1940). Most fruits, some tomatoes, and some other vegetables contain enough pectic substances to give a definite reaction with calcium. The extent to which the reaction occurs depends on a combination of physical and chemical factors. One such factor is the ratio of pectin to protopectin. According to Appelman and Conrad (1927) the disintegration of tomatoes during canning is greatest when the ratio of pectin to protopectin is greatest. Enzymatic demethoxylation of pectin to pectic acid probably takes place rapidly and if, at that point, calcium is available the pectate that is formed prevents the breakdown of cell structure. Degree of ripeness of the fruit or vegetable is an important factor, therefore, in the extent to which firming of the tissues can take place by means of calcium salts, since there is a direct relationship between ripeness and the amount of pectin present. The products used in the study reported here were harvested when they were considered ripe according to the practical judgment of the grower. Even a few hours, however, could probably make a difference in fruits and vegetables in which the amount of pectin is not great at any time. It is possible that, if the pectin content is high, there is less limitation in the range of degree of ripeness within which reaction with calcium takes place. The fact that actual degree of ripeness was not known for the products tested in this experiment may explain the inconsistency of results.

SUMMARY

Calcium chloride, at concentrations of 0.05, 0.07, and 0.09 percent of the material, was added to asparagus, rhubarb, strawberries, plums, gooseberries, and red raspberries, in order to find out what effect the calcium salt would have in helping to preserve firmness of tissue in

the canned product. Texture, flavor, and ascorbic acid content of the canned products were also evaluated. Flavor was not impaired by calcium chloride in concentrations less than 0.09 percent. The judges found strawberries, plums, and rhubarb "salty" at the level of 0.09 percent calcium chloride. Texture of plums, rhubarb, and raspberries was scored by the judges as being improved by the calcium treatment. Ascorbic acid content in strawberries, raspberries, and gooseberries, treated with calcium chloride, was higher than in the controls, but not in proportion to the amount of calcium salt added. Calcium chloride had a marked protective action on ascorbic acid in raspberries canned with water but not on those canned without water. Cuthbert raspberries had less ascorbic acid than Lathams, but not enough samples were used to affirm a definite varietal difference. Within one variety, the Lathams, the riper berries had a higher ascorbic acid content than those less ripe. Again, not enough samples were used to establish the difference. The foods kept for the longer period, 13 to 16½ months, had less ascorbic acid than the corresponding foods kept for a shorter time, nor did there seem to be any protective effect of calcium chloride.

Strawberries were firmed to a slight extent by calcium chloride addition, while raspberries canned with water showed a definite firming. The raspberries canned without sugar showed marked firming of tissue by calcium chloride, but the ones canned with sugar had a lower drained weight in the calcium-treated samples than in the controls. Rhubarb was softer when treated with calcium while the other products were scarcely affected. All the foods, except asparagus, had higher drained weights at the end of the longer period of holding than those kept 4½ to 6½ months.

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