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Correlation between Soaking Conditions, Cation Content of Cell Wall, and Olive Firmness during "Spanish Green Olive" Processing

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"Spanish green olives" in two important stages of their processing (pH 11—after sodium hydroxide treatment—and pH3—pH after fermentation) have been studied by adding increasing concentrations of sodium and calcium chloride to the soak solutions. Correlations among firmness, pH, and the concentration of the different cations were derived. Ca^{2+} at pH 11 showed a logarithmic response that changed to linear at pH 3. Na^{+} produced linear increases in texture only at pH 11, being ineffective at pH 3. High concentrations of sodium at pH 11 caused the calcium effect to change to a linear correlation. The results from this study show that calcium displaced sodium from the cell wall structure to a great extent but that there was very little decrease of calcium in the cell wall as a result of the presence of sodium, results that suggest two different ways of cell wall stabilization: one by formation of coordination complexes (only by calcium) and the other by electrostatic means (by both calcium and sodium).

Keywords: *Olive; cell wall; texture; processing; cations; competition*

INTRODUCTION

Texture is one of the most important organoleptic characteristics of a vegetable product. Although the concept "texture" is still poorly defined or understood (Jackman and Stanley, 1995), consumers have very clear expectations. The cell wall and middle lamella structure and composition are mainly responsible for texture quality. At present, most olive industries are undergoing product improvement to achieve higher consumer acceptability and lower processing plant losses due to inadequate firmness.

It has been widely accepted that one of the fastest and easiest methods to modify texture is to add certain cations to the soaking liquids. However, the effects acheived depend on the nature of the cation and the process, both of these factors having very different effects on the cell walls. Calcium is known to have a very strong texture-increasing effect and even retards softening during storage (Tang and McFeeters, 1983; Fleming et al., 1987; Brenes et al., 1994). This divalent cation could act by neutralizing negative charges created in pectin chains via different mechanisms during processing and by forming stable complexes with them. This reorganization of the pectic structure makes hydrolysis using polygalacturonases impossible (Buescher et al., 1979) and even leads to the inhibition of Cx-cellulases (Buescher and Hudson, 1984). Calcium also reduces microbial growth during storage at several temperatures (Izumi and Watada, 1994). There is only one reported case where calcium produced losses in texture: when the plant tissue was heat-treated, calcium increased the β-elimination rate in pectin chains, which was the principal reaction of the softening process (Keijbets and Pilnik, 1974; Van Buren et al., 1990; Sajjaanantakul et al., 1993). Sodium has always been considered as a firmness-decreasing cation and also to increase softening rates. Its slight refirming effect at high pH levels is lost when pH values decrease (Van Buren et al., 1988). The softening effect is caused by the promotion of β-elimination (Van Buren et al., 1990) and/or the displacement of calcium cations from the cell wall structure (Van Buren, 1984). Studies on this competition between cations are needed in order to clarify the mechanisms of the different effects each cation has on cell wall structure.

Olives processed as "Spanish green olives" undergo very strong chemical treatments that produce an intense deesterification of cell wall pectins (Jiménez et al., 1995, 1996), leading to a product that is very sensitive to cations. Previous studies on other types of olives, such as black ripe olives (by oxidation) and natural black olives (Fernández et al., 1975; Mínguez et al., 1978; Durán et al., 1986; García et al., 1994), demonstrated a positive effect of calcium on texture but firmness losses using sodium in natural black olives (without chemical treatment). Spanish green olives, as has been pointed out above, are more sensitive to cations because of the sodium hydroxide (lye) treatment. In fact, sodium cations led to important texture increases just after lye treatment (pH of the flesh = 11−12) and after fermentation (pH 3−4) (Jiménez et al., 1995). Green olive producers suffer marked economic losses during olive handling because of inadequate firmness just after lye treatment or fermentation. Green olives undergo many handling changes of containers and of soaking liquids (lye treatment and washes in 16 000 L tanks, fermentation in sunken vats, storage, sorting and size classification, stoning, stuffing, and packing), which causes beating, bruising, and breakage of fruits. The aim of this work has been to determine the usefulness of cation additions during green olive processing at both pH 11 and 3 and to study their role in cell wall structure. It is important to establish mathematical models between cation concentration and texture that are useful for industrial applications.

EXPERIMENTAL PROCEDURES

Olive Processing. Olive fruits (*Olea europaea* ssp. *arolensis* var. Manzanilla) harvested in the province of Seville, Spain, were processed as "Spanish green olive" style as described previously (Jiménez et al., 1995, 1996). Two experiments (1 and 2) were carried out on different olive fruit batches, which led to different final products.

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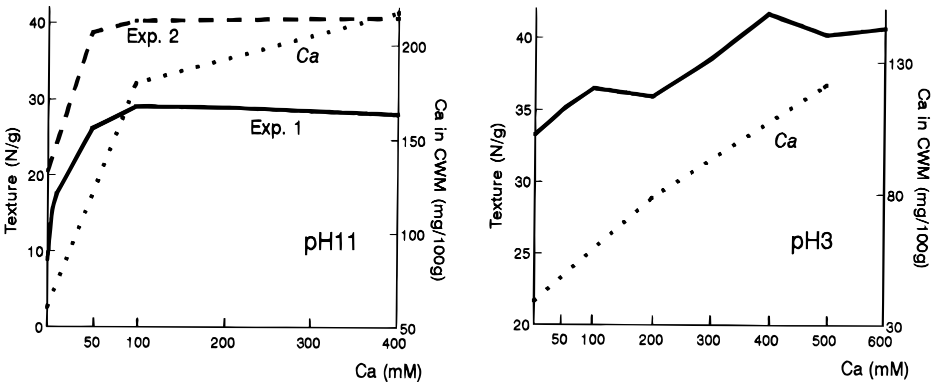

Figure 1. Effect of calcium ions on olive texture at two pH values. Dotted lines represent the calcium content of cell wall material (CWM) expressed as mg/100 g CWM (Y_2 axis).

Soaking Conditions. After being washed, the olives (flesh pH 11) were divided into two portions: the first was directly packed into 16-Reference jars (445 mL capacity) with tap water and sodium and/or calcium chloride added to attain the following concentrations in the soak solutions. (a) To study cation effects separately, the concentrations of calcium chloride were 0, 5, 10, 50, 100, 200, 300, 400, 500, and 600 mM and the concentrations of sodium chloride were 0, 0.05, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 1, 1.5, 2, 2.5, and 3 M. (b) To study the competition between cations, the concentrations of calcium chloride were 0, 50, 100, 200, 300, 400, and 500 mM and the concentrations of sodium chloride were 0, 0.5, 1, 1.5, 2, 2.5, and 3 M.

The second portion was acidified to pH 3 with HCl. After equilibrium, the same amounts of sodium and/or calcium chloride were added. Both batches were stored at 4 °C until analysis. Before texture measurements, samples were kept at room temperature for 48 h.

Texture Determination. The fruit texture was measured using a texturometer Instron Model 1011 fitted with a Kramer shear-press cell. The operating speed was set at 200 mm/min, and the force scale was 0−500 N. The results given are the means of 15 replicates.

Preparation of Cell Wall Material as the Alcohol-Insoluble Residue (AIR). Duplicate 15 g samples of the fruit flesh were homogenized at top speed in an Ultra-Turrax T-25 (Janke & Kunkel, IKA-Labortechnik) with four volumes of 96% ethanol. After centrifugation (1300*g*, 10 min), samples were washed again with 80% ethanol. The pellets were resuspended several times in acetone until supernatants were colorless. The dried final residue (AIR) was the starting point of cation content determinations.

Ashing Treatment. Around 0.3 g of AIR from each sample were weighed into porcelain capsules and ashed for 2−3 days with several deionized water additions in a Heraeus oven at 450 °C. The white ashes were weighed and prepared for Ca^{2+} and Na^+ analysis.

Ca^{2+} and Na^+ Determinations. White ashes were washed three times with 2 mL 2 N HNO_3, vacuum filtered, and diluted in a 25 mL volumetric flask with deionized water (soln A). Na^+ was determined directly in this solution by flame spectrophotometry in an EEL photometer with air/butane flame. A standard curve of NaCl was plotted between 0 and 100 ppm.

A quantity of 1 mL of soln A was transferred to a 50 mL volumetric flask, adding 2 mL of 5% lanthanum chloride solution and diluting to volume with deionized water. Ca^{2+} was determined in this solution by atomic absorption in a Perkin-Elmer Model 703 spectrophotometer at 422 nm wavelength with an air/acetylene flame. Readings were compared to a standard curve between 5 and 30 ppm.

Statistical Analysis. The data were statistically studied by analysis of variance. Means were compared with Duncan's multiple range test ($P < 0.05$). Regression analysis was performed by simple regression with confidence and prediction intervals of 95%.

RESULTS AND DISCUSION

Both calcium and sodium ions increased olive texture in general, but the way by which the texture was recovered depended on the cation, its concentration, and the pH in the soak solutions. The presence of calcium had a very marked effect (Figure 1). At pH 11, the maximum texture was reached with a 100 mM concentration in both experiments, and increasing amounts did not produce significant changes. It is interesting to note that the increase in texture did not depend on its initial value but was a fixed increment, 20 N/g; in experiment 1 firmness increased from 10 to 30 N/g and in experiment 2 from 20 to 40 N/g.

The response to calcium concentrations showed a clearly logarithmic correlation. Between 0 and 100 mM, the values were very approximately predicted by the following regression equation:

$$T = T_0 + 10.16 \log[\mathrm{Ca}], \quad r^2 = 99.49 \qquad (1)$$

where T = texture at each calcium concentration, T_0 = initial texture at pH 11, and [Ca] = calcium concentrations in brine (mM).

At pH 3, the first thing to be noted was that the initial texture was higher than at pH 11 (the olives from the experiment at pH 3 were from the same lye treatment as those from experiment 2 at pH 11, so the increase from 20 to 33 N/g was due to the decrease of pH). The presence of a higher concentration of $[H^+]$ in the soak solution gave rise to a marked recovery of firmness, the pH value being another important factor to take into account. This low pH value produced a change in the response to calcium; there were significant increases up to 400 mM Ca (a higher concentration than at pH 11), but in this case the response was linear, not logarithmic, according to the equation

$$T = T_0 + 0.02[\mathrm{Ca}], \quad r^2 = 89.98 \qquad (2)$$

where T = texture at each calcium concentration, T_0 = initial texture at pH 3, and [Ca] = calcium concentration in brine (mM).

Studying softening rates of vegetable products during conservation in brine and canning, other authors have concluded that calcium diminishes softening rates, and its effect is more intense at high pH levels (McFeeters and Fleming, 1991; García et al., 1994), even when pectinolytic enzymes were added to brines (Fleming et al., 1987).

The calcium content of the cell wall material was analyzed by atomic absorption (Figure 1). Three samples

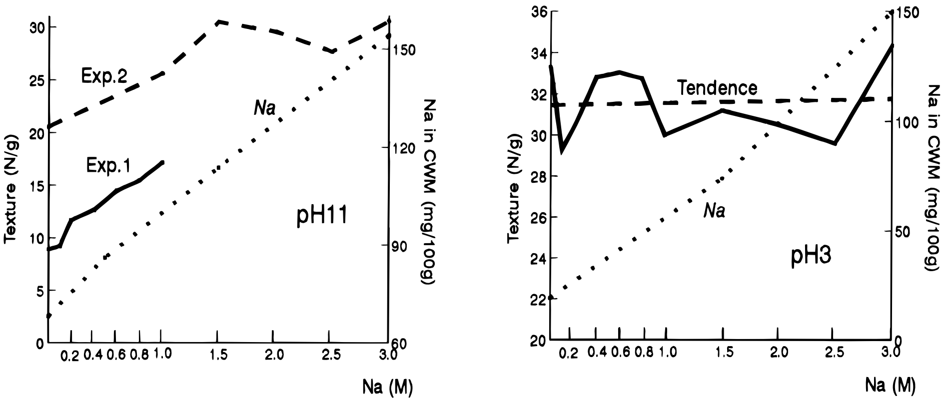

Figure 2. Effect of sodium ions on olive texture at two pH values. Dotted lines represent the sodium content of cell wall material (CWM) expressed as mg/100 g CWM (Y_2 axis).

were chosen for each experiment, at low, medium, and high concentrations of the studied cation. At both pH values, the absorption of calcium by the cell wall was similar to the response of texture; at pH 11, the content of the cell wall calcium sharply increased up to 100 mM Ca in the soak solution, and then it continued increasing but at a slower rate. The proportion of calcium in the cell wall not involved in texture (calcium stabilized by proteins, organic acids, and other charged molecules) seems to be very low because when texture reached its maximum, calcium continued being fixed, but it only represented 17% of the total calcium. At pH 3, besides the lower level of calcium in the cell wall, its penetration into the wall was more gradual, as was the increase of firmness. It seems as if the low pH leads to a positively charged environment that hinders the entry of calcium into the cell wall.

There were very good correlations between actual (experimental) and calculated values of firmness at both pH values, the relative differences being lower than 10%. This confirmed the mathematical correlation between texture and calcium in soak solutions, with only the regression model varying: logarithmic at pH 11 and linear at pH 3.

When sodium chloride was added to the soak solution in the absence of calcium, the maximum texture value was reached at a sodium level much higher than with calcium. At pH 11, the firmness reached its maximum with 100 mM calcium (as has been described above), but with sodium a concentration of 1.5 M was needed (Figure 2), and even at this concentration the final texture was lower than with calcium. At pH 11, the response was clearly linear up to a concentration of sodium in brine of 1.5 M, and above this the firmness did not suffer significant changes. The regression equation was

$$T = T_0 + 6.5[\mathrm{Na}], \quad r^2 = 96.92 \tag{3}$$

where T = texture at each sodium concentration, T_0 = initial texture at pH 11, and [Na] = sodium concentration in brine (M).

The correlation between actual and calculated values has been studied. There are very low variation values (≤10%), which indicates the closeness of the linear model.

The response of the cell wall to sodium at pH 3 was not so clear (Figure 2). There was no correlation between the evolution of texture and sodium in the cell wall, but the trend suggested that the presence of sodium in soak solutions did not produce any change; the cell wall had been equilibrated in the presence of a high concentration of cations (protons) so that the texture-increasing effect of sodium had been anulled (Van Buren et al., 1988). Sodium and protons seemed to have only an electrostatic role in texture recovery.

Table 1. Regression Equations of Texture Values at Different Sodium Levels and pH 11[a]

Na^+ concn (M)	equation[b]	r^2	Ca^{2+} concn range (mM)
0	$T = T_0 + 10.16 \log[Ca^{2+}]$	99.49	0−100
0.5	$T = T_0' + 6.78 \log[Ca^{2+}]$	97.16	0−100
1.0	$T = T_0'' + 0.13[Ca^{2+}]$	99.33	0−100
1.5	$T = T_0''' + 0.07[Ca^{2+}]$	99.92	0−200
2.0	$T = T_0''' + 0.06[Ca^{2+}]$	94.68	0−300
2.5	$T = T_0''' + 0.04[Ca^{2+}]$	93.49	0−300
3.0	$T = T_0''' + 0.02[Ca^{2+}]$	71.77	0−400

[a] Last column expresses the calcium concentration between which the equations are applicable. Higher concentrations do not produce significant changes in texture. [b] $[Ca^{2+}]$ in mM.

The results obtained by flame spectrometry to quantify sodium in the cell wall are very interesting. At pH 11, the slope of the increase of sodium concentration in the wall was very similar to that of texture, but when the latter stopped increasing, the amount of sodium continued to do so as before. Na^+ must be fixed in the wall in locations that have little or no effect on texture, and its level in the wall only depends on its concentration in the soak solution. From the figure for pH 3, the scant role of Na^+ in texture can be appreciated. The tendency of texture was to a constant value, but sodium in the wall increased as the concentration in the medium went up. It could be concluded, therefore, that at low pH values there was no relationship between sodium concentration and texture.

The presence of both cations in the soak solutions caused the cell wall response to each cation to change. Olives at both pH values were packed into jars with Na^+ concentrations between 0 and 3 M and Ca^{2+} between 0 and 500 mM to study their competition for negative charges and other active points, and the evolution of texture.

At pH 11, the presence of Na^+ and Ca^{2+} at different concentrations in the soak solutions produced some changes in the response of texture to cations. In Table 1 the regression equations are presented, including the range of concentrations in which these equations are suitable. It is very important to note that the type of regression changed when the concentration of sodium increased. Until Na^+ reached 1 M there was a logarithmic correlation, but above this concentration it was linear as was the case at low pH values. In addition,

Table 2. Regression Equations of Texture Values at Different Sodium Levels and pH 3

Na^+ concn (M)	equation[a]	r^2
0	$T = T_0 + 0.02\ [Ca^{2+}]$	89.98
0.5	$T = T_0 + 0.017\ [Ca^{2+}]$	87.73
1.0	$T = T_0 + 0.018\ [Ca^{2+}]$	76.99
1.5	$T = T_0 + 0.02\ [Ca^{2+}]$	43.17
2.0	$T = T_0 + 0.019\ [Ca^{2+}]$	77.89
2.5	$T = T_0 + 0.02\ [Ca^{2+}]$	76.88
3.0	$T = T_0 + 0.016\ [Ca^{2+}]$	79.45

[a] $[Ca^{2+}]$ in mM.

there were other changes in the regression parameters: slope and origin ordinate. In logarithmic correlations, by increasing sodium from 0 to 0.5 M, the slope decreases from approximately 10 to 6. In the linear ones the same relationship was found: in general, increasing concentrations of sodium produced a decrease in the slope of texture recovery, and the maximum was obtained at higher Ca^{2+} concentrations, as is indicated in the last column of Table 1. At each Na^+ level the logarithmic and linear regressions were studied (the results presented in Table 1 were the equations with the best r^2 values) and the evolution of the slopes also responded to a regression equation, with a logarithmic or linear correlation depending on the series studied:

$$\text{linear series} \quad S_{Na} = 0.17 - 5.42 \times 10^{-5}[Na] \qquad r^2 = 96.49 \quad (4)$$

$$\text{logarithmic series} \quad S_{Na} = 10.44 - 1.77 \log[Na] \qquad r^2 = 88.07 \quad (5)$$

where S_{Na} = slope of texture increases with calcium as a function of Na^+ concentration and [Na] = sodium concentration in soak solutions (mM).

As far as the origin ordinates of the equations presented in Table 1 are concerned (T_0, T_0', T_0'', and T_0'''), it is interesting to note that T_0 was the initial texture at pH 11 (without Na^+ or Ca^{2+} added to soak solutions) and the rest of the ordinates could be calculated from eq 3, which relates texture with sodium levels. Above 1.5 M Na^+ this parameter is constant (T_0''') because at this level the maximum texture was reached (Figure 2). This change in correlation from logarithmic to linear could be the reason other authors (Durán et al., 1986), working with "natural black olive" style, concluded that calcium could be useful only if sodium were present at low concentrations in brine; with higher concentrations of the monovalent cation there must be a displacement of calcium by sodium, thereby anulling the effect of the former. However, in the present study of "Spanish green olives", as will be described below, it has been shown that the displacement is minimal and that calcium continued being effective even with high sodium concentrations in soak solutions (it is important to bear in mind that the olives studied in this work are lye-treated—unlike "natural black olives"—and therefore more sensitive to cations).

As it was commented previously (Figure 2), the sodium content of the cell wall did not seem to have any effects on texture at pH 3. This explains the results presented in Table 2: the presence of sodium at different concentrations did not affect the response of texture to calcium. Both slope and origin coordinate were constant, thereby confirming the results shown in Figure 2.

The clearest evidence of competition between sodium and calcium was obtained by quantifying their content in cell wall material using flame spectrometry and atomic absorption spectrophotometry, respectively (Figures 3 and 4). Figure 3 summarizes the displacement of sodium by calcium in the cell wall structure. This was very marked, varying between 90% at pH 11 and Na 0 M, and 47% at pH 3 and Na 1.5 M. In all the conditions, the evolution of firmness was very similar to that shown by the calcium content in the cell wall material, as described above. By comparison of the upper (pH 11) and lower (pH 3) subfigures, it is noteworthy that the decrease of pH involved a decrease in the initial and final amounts of both sodium and calcium in the cell wall; protons obstructed the entrance of other cations into the cell wall structure. By comparison of the subfigures on the left (low sodium) with those on the right (high sodium), it can be seen that the final level of calcium also decreased when there was a high concentration of sodium in the soak solution (13%−25% decrease).

Figure 4 represents the displacement of calcium by sodium. In this case, only when there were no other added cations (pH 11, Ca 0 M), did the texture response parallel the increase of sodium. In the other three conditions, firmness showed the same behavior as Ca^{2+} concentration in the wall. The final level of Na^+ was affected very little (0%−4% decrease) by the other cations, protons, or calcium, and its content in the cell wall continued to increase as long as the concentration in the soak solution was going up. However, these high levels of sodium did not give rise to an intense displacement of calcium as described above, only a 40%−10% decrease (depending on the medium conditions). It is important to bear in mind that the maximum outer concentration of sodium (3 M) was much higher than that of calcium (0.5 M) and it is unlikely that the displacement caused was much lower.

FINAL REMARKS

Green olives, after lye treatment or under storage conditions, are very sensitive to the presence of cations in the medium. Both cations studied (calcium and sodium) and pH had a texture-increasing effect, but the mechanisms by which they had their effect seemed to be very different.

At pH 11, calcium had the greatest effect on texture. It showed a logarithmic response at very low concentrations. As was concluded in previous papers (Jiménez et al., 1994, 1995, 1996), the degree of pectin esterification decreased greatly during lye treatment, these polymers being negatively charged after olive washes (pH of the medium between 11 and 12). Although the presence of the other cations caused the calcium content in the cell wall to decrease, the texture reached the same values. There must be some locations that lead to texture increases by electrostatic means (places that could be occupied by monovalent and divalent cations) and others that need divalent cations, because they constitute coordination complexes (Anthonsen et al., 1972; Taiz and Zeigler, 1991). This demonstrates the inadequacy of the "egg-box" model (Grant et al., 1973) for explaining the cation effect on texture (McFeeters and Fleming, 1989). When calcium is the only cation available in the soak solution, it occupies both types of locations, and this leads to a strong and fast texture recovery. When monovalent cations are added, they compete with calcium for ionic places but never by complex formation, so calcium continues giving rise to marked increases in texture. This explains why only a

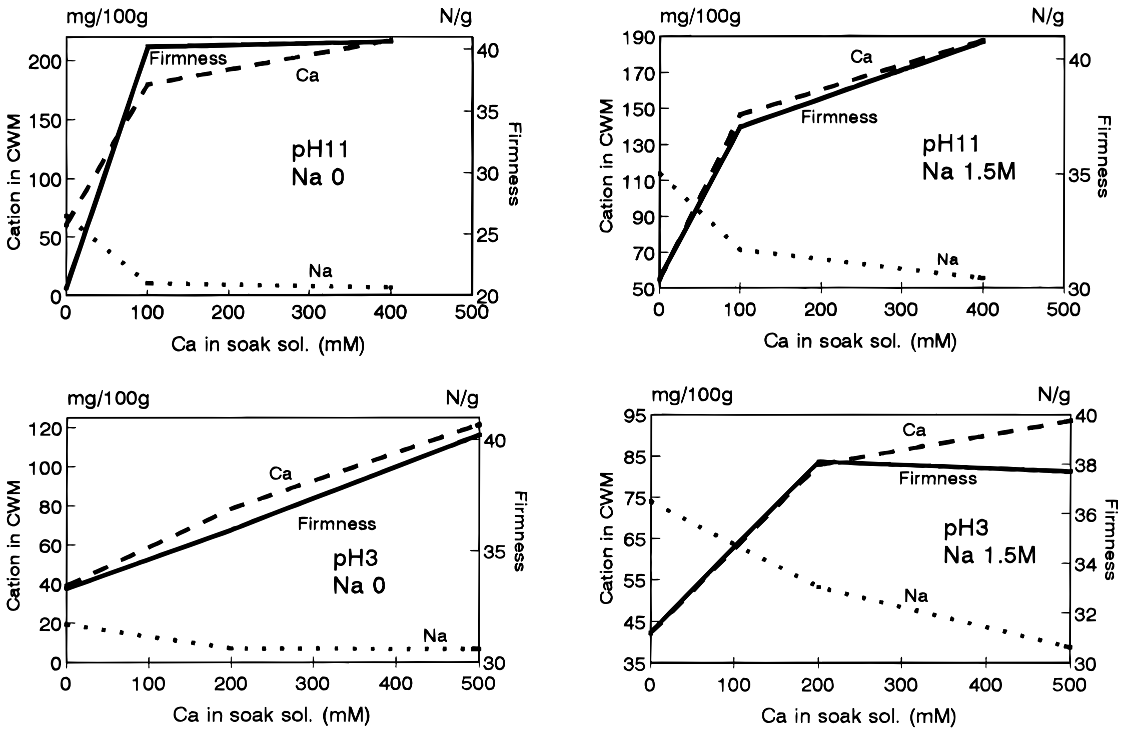

Figure 3. Evolution of firmness (N/g) and sodium and calcium content (mg/100 g) of cell wall material (CWM) at different soaking conditions (pH and sodium concentration) depending on calcium concentration in soak solutions.

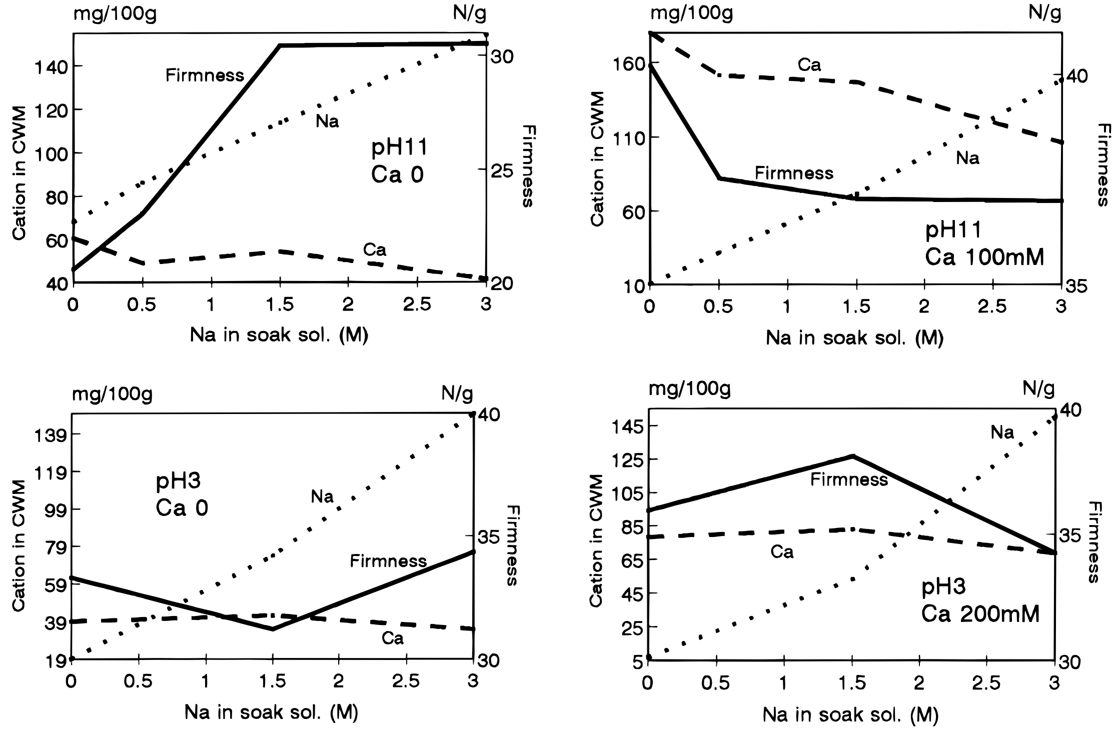

Figure 4. Evolution of firmness (N/g) and sodium and calcium content (mg/100 g) of cell wall material (CWM) at different soaking conditions (pH and calcium concentration) depending on sodium concentration in soak solutions.

low proportion of calcium in the cell wall could be displaced by protons or sodium, the calcium which is ionically stabilized. At pH 11, the cell wall is more sensitive to different ionic conditions in the medium. As was pointed out above, a high proportion of acidic polysaccharides are ionized at this pH, and even neutral polysaccharides (galactomannans, which are present in the olive cell wall) can, in these conditions, accept calcium cations (Kolb and Kunkel, 1994). At low pH values, the ionic locations are occupied by protons. Calcium still has an effect, unlike sodium, which has only an electrostatic function. This ionic effect is considered to be only a minor factor affecting vegetable texture (Van Buren, 1984). Sodium is present in higher and higher amounts in the cell wall as the outer concentration continues increasing, but this has no effect on firmness; monovalent cations can be stabilized by other charged molecules that are natural components of the cell wall but that do not have any effects on texture.

The response of olive cell walls has been mathematically studied by these experiments, and it shows a very clear behavior. The resulting models have shown to be highly suitable for predicting the evolution of firmness depending on soaking conditions. Their simplicity makes them very easily applicable by green olive industries, which are nowadays improving their products.

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