Thermal Degradation of Green Asparagus Texture

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ABSTRACT

A cutting cell was developed to evaluate the texture of green asparagus by measuring its resistance to being cut with a wire. The cell was used in conjunction with a universal texturometer and improved on the single-point method of the Wilder fibrometer. Experimental conditions were determined for using the cell to measure the cutting resistance of asparagus subjected to different extents of heat treatment. Better discrimination between samples was obtained than with a Kramer cell. The fresh asparagus spears were heated at temperatures between 70 and 100°C for different lengths of time and the kinetics of the degradation of texture was studied. A biphasic (two-component) behavior was observed with each component displaying first-order kinetics. The kinetic parameters calculated by measuring the texture with the wire cell (cutting at a position 5 cm from the tip of the asparagus) were $E_{ab} = 9.56$ and $E_{ab} = 20.43$ kcal/mol (activation energy for components A and B), and $k_{ab85} = 1.047$ and $k_{ab85} = 0.057$ min$^{-1}$ (rate constants for A and B of asparagus heated at 85°C). When the texture was determined by measuring the shear force with a Kramer cell, the parameters estimated were $E_{aa} = 23.41$ and $E_{aa} = 18.32$ kcal/mol, and $k_{aa85} = 0.25$ and $k_{aa85} = 0.025$ min$^{-1}$. Both the wire cell cutting method and the Kramer shear-press method are suitable for evaluating the degree of thermal softening of green asparagus heated to temperatures between 70 and 100°C.

Key words: Asparagus texture, thermal degradation, kinetics

Production of green asparagus in Spain has increased in recent years due to increased consumption of fresh asparagus and the manufacture of canned asparagus. The color and stronger flavor of green asparagus are more reminiscent of the wild product than those of white asparagus and are appreciated by a substantial sector of consumers. However, the chief reason for the increase in production is the fact that the end product is cheaper than white asparagus, because harvesting is easier and can be done mechanically, and less fiber develops during transport and prestorage, so that peeling is not necessary (13).

The texture of a vegetable is determined by the structure and composition of its cellular tissue, and the cell wall is one constituent of the tissue which most affects this property. The cells that make up the wall consist of pectic substances, hemicellulose and lignin among others (14). The texture of asparagus is directly related to its development of fiber. Fibrousness is due to the lignification of fibrovascular clusters at ambient temperature during the first few hours after harvesting; it is a process controlled by enzymes that is inherent in ripening (7). The acceptance or rejection of this vegetable by consumers largely depends on its texture, so that fibrousness is one of the most important quality factors (12).

Consumers increasingly demand products that maximally retain their nutritional and sensory characteristics, and texture is one of the sensory characteristics most affected by thermal processing. In this context, canned green asparagus has a very soft consistency and undergoes a significant loss in weight (4). These characteristics can be improved by optimizing the thermal processing of the product, and for this it is essential to have a suitable method for measuring texture and establishing the kinetics of its degradation by heat treatment.

The methods most commonly used for determining asparagus texture fall into two groups (4, 21, 22): semiquantitative, such as the Wilder fibrometer method, and quantitative, such as the Kramer shear-press method. The Wilder fibrometer is the method generally used by manufacturers and is included in quality regulations in Spain (1) and in those of the Department of Agriculture in the USA (18). It consists of a semiquantitative identification of the number of fibrous units per sample. The Kramer cell quantifies a mean value for the texture of the specimens making up a sample but not the fibrousness of an individual specimen.

The description of texture changes due to thermal processing can be studied by using kinetic models, as can chemical reactions. Two kinetic models are used to quantify the thermal softening of vegetable tissues (3): a first-order model ($n = 1$), where it is assumed that the rate of softening at a fixed temperature is proportional to the property value measured, and a two-fraction model ($n = 2$), where it is assumed that the vegetable tissue has two fractions, each
with its own kinetic parameters and each following a first-order model. The first fraction is rapidly degraded by heat and the second fraction, with a property called "thermal firmness," is more resistant to heat degradation (2).

The first of our objectives focused on the development of a cutting wire cell for the quantitative determination of cutting force in order to measure the texture of individual asparagus specimens with an Instron press. For comparison, the measurements were also determined by the standard Kramer shear-press. Both methods were used to estimate the kinetic parameters for the degradation of asparagus fibrousness by using the two-fraction model.

MATERIALS AND METHODS

Green asparagus

Fresh green asparagus (Asparagus officinalis L. var. Mary Washington) was obtained from the El Santo Cristo Cooperative in Navarres, Valencia, Spain. The asparagus were harvested and we received them within 24 h. The vegetables were 11 to 14 mm in diameter (classified as "thick") and 18 to 20 cm in length, with closed tips. The asparagus was washed with ordinary water to eliminate soil and other extraneous substances adhering to it and then refrigerated at 4 to 6°C at a relative humidity (RH) of 95% for a maximum of 4 days. The spears were cut to a length of 15 cm before the experiments were performed. Tests were also carried out on five different commercial brands of canned green asparagus purchased in local shops and similar in size to the fresh samples.

Development of the wire cell

The wire cell consisted of a steel strip 1 mm thick, cut in the form of an inverted U, the open ends of which were soldered to a steel wire. The wire was of various diameters: 0.25, 0.40, 0.50, and 0.80 mm (Figure 1a). The base consisted of a slot designed so that it could be changed to different widths (Figure 1b), with guides at the sides to direct the steel strip towards the slot. Tests were carried out with slot widths of 0.8, 1, 1.5, and 2 mm.

Measurement of texture

An Instron 6021 press was used. Preliminary studies showed that the storage conditions (maximum of 4 days at 4 to 6°C and high RH) of the fresh samples do not affect the texture (P ≥ 95%), results which are consistent with those of other studies (8). A 100-N cross-head was used for the wire cell, and the maximum force in newtons required to cut the asparagus was measured at different distances from the tip: 2.5, 5, 7.5, 10, and 12.5 cm. Three speeds were tried for the cross-head: 200, 500, and 1,000 mm/min. For each heat-treatment batch, 30 asparagus specimens were measured. For the Kramer shear-press (standard cell with 10 blades), the asparagus was first cut into pieces 2.5 cm in length with the wire cell; 80 g of cut pieces was then placed randomly in the base of the Kramer cell and the maximum shear-force values were recorded. The cross-head used gave a maximum load of 5,000 N and was used at 200 mm/min. At least three determinations were made for each time-temperature combination.

Thermal treatment

Fresh green asparagus spears were blanched at 80°C for 2 min and immediately cooled by submerging them in a water and ice bath. They were left at room temperature until the thermal treatment was begun. Batches of 30 specimens were heated in a water bath under different combinations of temperature and time. The temperatures selected were 70, 80, 90, and 100°C. The asparagus was placed in small perforated stainless-steel mesh baskets and submerged in a water boiler heated by a steam jacket, with a specially designed system of forced recirculation of water. The boiler had a temperature control which acted on the steam intake to achieve a uniform temperature (±0.5°C) inside the apparatus. The heating times used were 3, 6, 9, and 12 min for temperatures of 70 and 80°C and 1.5, 4.5, 7.5, and 10.5 min for temperatures of 90 and 100°C. After each heat treatment the asparagus was quickly cooled by immersion in an ice-water bath and subsequently left at 20°C until the measurements were done.

The texture of the commercial canned samples was measured without any preliminary heat treatment.

Statistical and mathematical treatment of the results

In order to compare the mean values obtained for cutting force and shear-press force in the various samples of asparagus corresponding to different thermal treatments, a BMDP software program was used to perform analyses of variance and Tukey’s tests at a 99% confidence level. The software was also used to calculate a regression.
Estimation of kinetic parameters

The kinetics of thermal softening of vegetables can be described by the equation used in (11) (among others):

$$dF/dt = -k_tF^n,$$  \hspace{1cm} (1)

where \(k_T\) is the reaction rate constant \(\text{(min}^{-1}\)),
\(F\) is total firmness at time \(t\) \(\text{(maximum force at time} \ t)\) \(\text{(N)},
\(n\) is the reaction order, and
\(t\) is time \(\text{(min)}\).

The dependence of \(k_T\) on temperature can be described by the Arrhenius model:

$$k_T = k_R \exp \left[-\frac{E_a}{R(1/T - 1/T_R)}\right],$$  \hspace{1cm} (2)

where \(k_R\) is the reaction rate constant \(\text{at reference temperature (min}^{-1}\)),
\(E_a\) is the activation energy \(\text{(kcal/mol)},
\(R\) is the ideal gas constant, \(1.987 \text{cal/(mol } \cdot \text{K)},
\(T\) is temperature \(\text{(K)}\), and
\(T_R\) is reference temperature \(\text{(K)}\).

For isothermal conditions, Equation 1 can readily be integrated and Equation 2 substituted, i.e.,

$$F = \left[F_0^{(1-n)} - (1 - n) k_R \exp \left[-\frac{E_a}{R(1/T - 1/T_R)}\right]\right]^{1/(1-n)},$$  \hspace{1cm} (3)

where \(F_0\) = initial firmness \(\text{(N)}\). A nonlinear regression was made with the whole sets of data to estimate \(n\) and \(F_0\) (Equation 3).

The kinetics of asparagus softening was analyzed by the two species--two mechanism mode \((6)\) in which two components, \(A\) and \(B\), following first-order kinetics, contribute to firmness:

$$\begin{align*}
A & \rightarrow A_o + F_a \\
B & \rightarrow B_o + F_b
\end{align*},$$

where \(A\) is firmness due to component \(A\) at time \(t\),
\(B\) is firmness due to component \(B\) at time \(t\),
\(k_a\) is the rate constant for loss of firmness in component \(A\), and
\(k_b\) is the rate constant for loss of firmness in component \(B\).

For \(n = 1\), integration of Equation 1 yields:

$$A = A_0 \exp \left(-k_T t\right),$$  \hspace{1cm} (4)

$$B = B_0 \exp \left(-k_T t\right),$$  \hspace{1cm} (5)

where \(A_0\) is initial firmness due to component \(A\),
\(B_0\) is initial firmness due to component \(B\), and
\(F_0 = A_O + B_O\).

At any time the total firmness is due to \(A\) and \(B\) \((F = A + B)\):

$$F = A_0 \exp \left(-k_T t\right) + (F_0 - A_0) \exp \left(-k_T t\right).$$  \hspace{1cm} (6)

A nonlinear regression with Equation 6 was performed to estimate kinetic parameters \(k_T\) and \(k_T\). A logarithmic expression of Equation 2 was used to estimate \(E_{oa}\) and \(E_{ob}\) (activation energy of firmness degradation in components \(A\) and \(B\) respectively) and \(k_{oa}\) and \(k_{ob}\) (rate constant for loss of firmness in components \(A\) and \(B\) at reference temperature respectively) for each measuring cell.

RESULTS AND DISCUSSION

Preliminary tests with the wire cell

The Wilder fibrometer is widely used but offers only qualitative results. We therefore developed a quantitative method which uses cutting forces for the determination of asparagus texture and which has certain features in common with the Wilder fibrometer: (i) the spear is cut crosswise at various distances from the tip, and (ii) the cutting system is based on the use of a steel wire. The features that distinguish the wire cell method are (i) the steel wire used has a smaller diameter than the one used in the fibrometer, (ii) the load applied is not static, (iii) the cutting force of each asparagus specimen is recorded (so that the method is quantitative), and (iv) a constant cutting speed is used.

The tests were performed with samples subjected to different heat treatment conditions in order to study the effects of the diameter of the steel wire, the width of the slot in the base plate and the speed of the cross-head.

Effect of the diameter of the wire. A steel wire with a diameter of 0.5 mm was selected as being the most suitable for the cutting operation. A wire with a larger diameter (0.8 mm) has a greater tendency to draw fiber into the slot, giving rise to erroneous results. On the other hand, thinner steel wires (0.25 and 0.40 mm in diameter) make cleaner cuts but have a greater tendency to bend, introducing errors into the cutting-force values recorded and even breaking in the case of hard or very fibrous asparagus.

Effect of the width of the base-plate slot. A slot width of 1.5 mm was selected for performing the measurements. A wider base plate slot (2 mm) encourages the introduction of fiber into the slot, while narrower slots (0.8 and 1 mm) lead to problems of scraping against the metal piece holding the wire.

Effect of the speed of the cross-head. If the cross-head descends faster, a cleaner cut is obtained. Consequently, the speed selected for the test was 1,000 mm/min, the maximum obtainable with the equipment.

Comparative study of the wire cell and the Kramer shear-press cell

The ability of the wire cell and the Kramer shear cell to differentiate the thermal softening of asparagus was studied by measuring the cutting force and the shear force. The samples used consisted of fresh asparagus heated in a bath of boiling water for 3, 5, and 9 min, and 5 samples of commercial canned asparagus.

The wire cell was used to measure the cutting resistance of a minimum of 20 spears for each thermal treatment. The cuts were made 2.5, 5, 7.5, 10, and 12.5 cm from the tip. The cuts 10 and 12.5 cm from the tip produced widely scattered results, probably due to excessive extraction of the fibre that occurs in these more fibrous parts of the spear. Therefore,
TABLE 1. Measurements of shear resistance by the wire cell and the Kramer cell of fresh spears of green asparagus heated for different lengths of time and cut at different distances from the tip, and commercial canned green asparagus

<table>
<thead>
<tr>
<th>Asparagus sample (min at 100°C)</th>
<th>Wire (cut, cm from tip)</th>
<th>Kramer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2.5)</td>
<td>(5.0)</td>
</tr>
<tr>
<td>Fresh (3)</td>
<td>6.2 (1.7)a</td>
<td>6.0 (1.0)α</td>
</tr>
<tr>
<td></td>
<td>4.6 (1.2)b</td>
<td>6.5 (2.0)α</td>
</tr>
<tr>
<td></td>
<td>2.8 (1.4)c</td>
<td>4.4 (2.6)β</td>
</tr>
<tr>
<td>Canned A</td>
<td>0.8 (0.4)d</td>
<td>1.2 (0.5)c</td>
</tr>
<tr>
<td>B</td>
<td>0.7 (0.3)d</td>
<td>0.7 (0.2)c</td>
</tr>
<tr>
<td>C</td>
<td>0.7 (0.5)d</td>
<td>0.9 (0.4)c</td>
</tr>
<tr>
<td>D</td>
<td>0.9 (0.2)d</td>
<td>0.7 (0.2)c</td>
</tr>
<tr>
<td>E</td>
<td>0.8 (0.3)d</td>
<td>0.9 (0.5)c</td>
</tr>
</tbody>
</table>

*Means within columns followed by the same letter are not significantly different at the 5% level according to Duncan’s multiple range test.

The analysis of the results obtained with the Kramer shear-press showed that, although the samples were grouped in descending order of shear force, there was not complete discriminate between the different treatments. Three groups were established with significant differences between the mean shear-force values corresponding to heating for 3 and 9 min and between these values and those of the commercial samples, which once again formed a single group without significant differences between the various brands.

**Kinetics of the thermal destruction of asparagus texture**

Blanched asparagus were cut into pieces 2.5 cm in length and the texture was determined by measuring the shear force with the Kramer cell; the mean shear force value obtained was 2,728 ± 300 N. It was not possible to determine the cutting force with the wire cell because the value of the resistance was high and the wire broke or bent before cutting the spear, producing erroneous readings.

In order to determine the order of the texture-degradation reaction, after heating the asparagus at different time-temperature conditions and determining their fibrousness with the wire cell and the Kramer shear cell, a nonlinear regression was performed with the data obtained with each of the two cells (Equation 3). The order of the reaction estimated for the Kramer shear-press cell was 2.21, and for only the values corresponding to cuts made 2.5, 5, and 7.5 cm from the tip were included in the study.

An analysis of variance was used to compare the mean values of the cutting force obtained with the wire cell for each cutting distance and the Kramer shear-press force for the samples subjected to heating at 100°C for different periods and for the commercial samples. The results are summarized in Table 1, which clearly shows that the cutting force values are higher for cuts made farther away from the tip and for longer heating times. At a distance of 2.5 cm from the tip, the cutting-force values for the various heat treatments are significantly different, providing four distinct groups: one group for each of the three heating times (3, 5, and 9 min) and a farther fourth group for the commercial samples. When the cut is made farther away from the tip (5 and 7.5 cm), discriminative ability is lost. The cutting-force values for a cut 5 cm from the tip do not provide significant differences between the results for heating times of 3 and 5 min, but do differentiate between these samples and those heated for 9 min and also the commercial samples. The cutting-force values for a cut 7.5 cm from the tip do not differentiate between the samples heated for 3, 5, and 9 min, but these cutting-force values are significantly different from the values for the commercial samples. For each of the three cutting distances the commercial samples form one single group.

The use of the wire cell together with the Instron press is a method that produces very good results for the instrumental evaluation of green asparagus texture, with cuts being made 2.5, 5, and/or 7.5 cm from the tip. Cutting 2.5 cm from the tip provides greater discrimination between different heat treatments, although with more severe treatments (as in the case of the commercial samples) problems can occur because the tips break easily and damaged or broken asparagus cannot be used for measuring at the 2.5-cm position. The data obtained from cutting at the 5-cm position provide better discrimination than those obtained at 7.5 cm and the typical deviations are fewer.

![FIGURE 2. Thermal degradation of asparagus firmness heated at 70 (●), 80 (■), 90 (▲) and 100 (▼) °C, measured with a wire cell (spear cut at 5 cm from tip) (A) and the Kramer cell (B).](http://meridian.allenpress.com/jfp/article-pdf/60/3/315/2322062/0362-028x-60_3_315.pdf)
TABLE 2. Rate constants $k_a$ and $k_b$ for loss of firmness in components A and B of fresh green asparagus heated at different temperatures and subjected to shear-force measurements with the wire cell (cut 5 cm from tip) or Kramer cell

<table>
<thead>
<tr>
<th>Asparagus heated at (°C)</th>
<th>Wire</th>
<th>Kramer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_a$</td>
<td>$k_b$</td>
</tr>
<tr>
<td>70</td>
<td>0.549</td>
<td>0.018</td>
</tr>
<tr>
<td>80</td>
<td>0.992</td>
<td>0.035</td>
</tr>
<tr>
<td>90</td>
<td>1.143</td>
<td>0.073</td>
</tr>
<tr>
<td>100</td>
<td>1.832</td>
<td>0.207</td>
</tr>
</tbody>
</table>

*Estimations of rate constants from nonlinear regression on Equation 6.

Asparagus subjected to shear-force measurements using the wire cell and the Kramer cell respectively, together with the best curves obtained by fitting the data for each temperature to Equation 6. Asparagus heated at 70 °C was 26.03 N. Huang and Bourne (6) reported that the two species–two mechanisms mode provides a good fit for the experimental data, and so a value of $n = 2$ was assumed.

Figures 2A and 2B show the experimental data for asparagus firmness degradation measured with the wire cell and the Kramer cell respectively, together with the best curves obtained by fitting the data for each temperature to Equation 6. The value of $F_0$ obtained from the nonlinear regression of Equation 3 for the wire cell ($F = 26.03$ N) was used to estimate $k_a$ and $k_b$ in this second nonlinear regression of Equation 6. For the Kramer cell, the value of $F$ obtained experimentally for the blanched asparagus was used ($F = 2,728$ N). Table 2 lists the rate constants estimated for the two cells. It can be seen that the rate constants increase as the heating temperature rises and that the rate constants for mechanism 1 ($k_a$) are generally 10 times greater than the rate constants for mechanism 2 ($k_b$). These results agree with the results reported by Huang and Bourne (6), who found for various vegetables that $k_b$ is 20 times or more greater than $k_a$.

The linear regression of $\ln k_a$ (or $\ln k_b$) versus $(1/T - 1/T_R)$ (Equation 2) was used to estimate $E_a$, $E_b$, $k_Ra$, and $k_Rb$ (Table 3) (Figure 3). The reference temperature used was $T_R = 85°C$, since this was the mean temperature assayed. The values of the rate constants ($k_{85} = 1.047$ and $0.025$ and $k_{85} = 0.057$ and $0.025$ min$^{-1}$) are within the range of constants estimated by other authors. Suzuki et al. (17) obtained $k_{op} = 0.516$ min$^{-1}$ when studying thermal softening of rice. The estimated values of $E_a$ (9.56, 20.43, 23.41, and 18.32 kcal/mol) are also similar to those found by other authors for the texture of various vegetables since, according to Lund (10), the $E_a$ values for the degradation of color, texture, and flavor vary between 10 and 30 kcal/mol. The rate of texture degradation of rice heated at 110 to 115°C Suzuki et al. (17) obtained $E_a = 8.83$ kcal/mol; Hayakawa et al. (5) obtained a value of $E_a = 22.6$ kcal/mol for the degradation of the organoleptic quality of green peas heated at 80 to 148°C; and Van Loey et al. (20) estimated a value of $E_a = 22.79$ kcal/mol for the loss of hardness of peas heated at 90 to 122°C.

The differences between the $E_a$ values obtained with the two cells may be due to their different ways of analyzing texture. The Kramer shear-press cell simultaneously applies different kinds of forces such as compression, shearing, and cutting, and it provides a mean value for the texture of a batch of previously cut asparagus, whereas the wire cell measures the cutting force of a single specimen of asparagus at a certain distance from the tip. The information provided by the wire cell is more specific, capable of quantifying the individual fibrousness of each asparagus specimen, and the value estimated depends on the area where the cut is made.

Huang and Bourne (6) obtained a value of $E_{aa} = 22.6$ kcal/mol and $E_{ab} = 12.9$ kcal/mol for the thermal softening of peas when heated at 104.4 to 121.1°C and a value of $E_{aa} = 15.2$ kcal/mol and $E_{ab} = 5.1$ kcal/mol for the thermal softening of a variety of carrot when heated in the same temperature range. These authors propose a mechanism for texture degradation consisting of two simultaneous first-order kinetic processes, where in the first process component A is rapidly degraded by heat and has a greater activation energy than component B, which is more resistant to heat. In the case of green asparagus previously blanched, when the texture is measured with the wire cell (cut at 5 cm), the $E_a$ value of the first kinetic process is less than that of the second process. These differences found with the wire cell by comparison with results for the Kramer cell and for other vegetables may be due to the particularly peculiar characteristics of asparagus, the blanching treatment, and the method of measuring its texture. Asparagus does not have a homogeneous texture either running along the length of the spear or from the outside to the inside. The hardness gradually increases from the extreme end of the tip to the base of the spear (15), and it has a fibrous sheath like a skin. Several authors reported that low-temperature blanching before

TABLE 3. Rate constants for loss of firmness in components A and B ($k_{55}$ and $k_{59}$) at reference temperature ($T_R = 85°C$) and activation energy of degradation of firmness in components A and B ($E_{aa}$ and $E_{ab}$) of fresh green asparagus subjected to shear-force measurements by the wire cell (cut 5 cm from tip) and Kramer cell

<table>
<thead>
<tr>
<th>Cell</th>
<th>$E_{aa}$ (kcal/mol)</th>
<th>$k_{55}$ (min$^{-1}$)</th>
<th>$r_a$</th>
<th>$E_{ab}$ (kcal/mol)</th>
<th>$k_{59}$ (min$^{-1}$)</th>
<th>$r_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire</td>
<td>9.6 ± 1.4</td>
<td>1.05 ± 0.07</td>
<td>0.9783</td>
<td>20.4 ± 1.9</td>
<td>0.057 ± 0.005</td>
<td>0.9913</td>
</tr>
<tr>
<td>Kramer</td>
<td>23 ± 3</td>
<td>0.25 ± 0.03</td>
<td>0.9873</td>
<td>18 ± 4</td>
<td>0.025 ± 0.005</td>
<td>0.9531</td>
</tr>
</tbody>
</table>

*Linear regression $\ln k_{ab}$ vs. $(1/T - 1/T_R)$.
canning or freezing increases thermal firmness, leading to significantly firmer textures in canned and frozen vegetables (9, 16). This increase in thermal firmness is due to the activation of the enzyme pectin methyl esterase (PME), an enzyme present but rather inactive at room temperature in most plant tissue that becomes active with heating between 50 and 80°C. PME catalyzes the demethoxylation of pectin substances; free carboxyl groups are formed, increasing the possibilities of calcium and magnesium binding between pectin polymers (19). Huang and Bourne (6) reported that the degradation mechanism which acts on component A is due to changes in pectic substances in the cell wall of the vegetable. Blanching and particularly the PME could have modified the composition of the pectic substances, increasing the thermal firmness and causing a slower texture degradation. This would explain why the component A has an $E_a$ value which is less than that of component B, the nature of which is unknown. This behavior is not apparent when the texture is measured with a Kramer cell because it does not measure fibrousness directly but rather the group of textural parameters as a whole.

ACKNOWLEDGMENTS

This work was supported by the CICYT (ALI84-0959-CO2-01). We are grateful to the Spanish Ministry of Education for supporting Carmen Rodrigo with a grant while she is working for her Ph.D. We also thank Cecilia Flores, Vicente Giner, and Vicenta Llorens for their technical assistance.

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