

# Gelatinization Profiles of Triticale Starch in Cookies as Influenced by Moisture and Solutes

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## ABSTRACT

Cereal Chem. 75(5):617–623

Starch physicochemical parameters and phase transitions were determined in flours of 10 advanced lines and cultivars of triticale (Cananea, Currency, Eronga, LA 24 Bve, LA 20 FCA, LA 83 FCA, Tatú, Tehuelche, Quiñé, and Yagan). Starch behavior was also analyzed during the baking of cookies prepared with triticale flours. Starch granule size, crystal type patterns, and size distribution were determined by light microscopy, X-ray diffraction, and gel-permeation chromatography, respectively. Two types and sizes of starch granules with characteristic A-form crystals were obtained in all samples tested. The Quiñé cultivar showed the lowest extent of starch crystallinity. Only a monophasic endotherm was found by differential scanning calorimetry for water content >50–60%. Gelatin-

ization temperature and enthalpy values varied significantly among samples. A biphasic endotherm was detected for water contents between 35 and 60%, and no endothermic transitions were observed for water levels <35%. Only one endotherm corresponding to starch gelatinization was detected in baked cookies prepared with five triticale flours. In all samples, the highest enthalpy of gelatinization of starch was detected for the cookie surface, whereas the highest gelatinization temperature was observed for the center. These differences may be attributed to the presence and content of the solutes in cookie dough and also to the degree of starch gelatinization during the cooking process.

Starch is the major component of triticale kernels, with contents varying from 64.9 to 73.8% (w/w), a range similar to that found in wheat and rye (Klassen and Hill 1971, Thomke et al 1987). The role of starch in bakery products has not received as much attention as that devoted to proteins, mainly because its properties are little affected by differences in cultivar or cultivation conditions (D'Appolonia et al 1978). Nevertheless, it has been known for several years that starch affects various baking stages: 1) it dilutes gluten to provide a more tender product; 2) it provides sugar for the fermentation process and for obtaining a suitable surface; and 3) it helps retain the gas formed, aids the absorption of water during gelatinization, and helps fix the film of gluten, avoiding dough collapse during cooling (Sandstedt 1961). Recent work by Petrofsky and Hosney (1995) showed that starch has an active role in determining dough rheological characteristics.

Several authors have reported that triticale flours are better for food products needing less gluten tenacity than they are for bread (Rodgers 1973, Tsen 1974, CIMMYT 1980, Peña and Amaya 1980). Recently, we showed that triticale advanced lines and cultivars (developed in improvement programs currently being conducted in Argentina) could become a good alternative in cookie production (Leon et al 1996). In that work, we also analyzed the influence of protein behavior on cookie quality. However, starch behavior during the preparation of cookies remains unclear. However, a significant relationship was found between the quality of flours used in cookie production and the amount of damaged starch (Abboud et al 1985, Rogers et al 1993).

Therefore, the aim of this study was to determine the physicochemical parameters and phase transition of the starch present in flours of 10 triticale advanced lines and cultivars and to analyze starch behavior during cookie production.

## MATERIALS AND METHODS

### Plant Materials

Flours were obtained from 10 advanced lines and cultivars of triticale grown in Campo Experimental of the Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Argentina. Lines

and cultivars under study (Table I) were sown by hand at the end of May in 3-m<sup>2</sup> parcels, and harvested by hand during December as lines or cultivars reached the optimal ripening level (plants totally yellow and grains hard and dry). Kernels were milled to extraction rates of 54–64% in a Brabender Quadrumat Jr. mill (Brabender, Duisburg, Germany).

### Chemical Analysis of Flours

Moisture, ash, and protein contents were determined by Approved Methods 44-15A, 08-01, and 46-11A (AACC 1995). Lipid content was obtained by extraction in hexane, followed by further elimination of the solvent by heating, according to IRAM 5593 Argentine standard (IRAM 1980). Starch content was calculated by subtraction, and all results were expressed on a wet-weight basis.

### Preparation of Starch

A pool of flours of the 10 triticale advanced lines and cultivars under study was collected. Starch was extracted at room temperature with 0.12N NH<sub>4</sub>OH (1:10, w/v, flour-to-solution ratio) (D'Appolonia et al 1978), and the dispersion was centrifuged at 12,000 × g for 5 min at room temperature. The pellet was retained and washed three times with 0.2N NH<sub>4</sub>OH. The starch obtained was vacuum-dried in an oven at 40°C until reaching constant weight. Unmodified wheat starch from Sigma Chemical Co. (St. Louis, MO) was used as a comparative sample.

### Gel-Permeation Chromatography

Gel-permeation chromatography was done in a 1.5- × 100-cm column packed with Sephacryl S-1000 (Pharmacia Fine Chemicals, Sweden) and using a constant flow (11 mL/hr) of 0.1N NaOH (Seneviratne and Biliaderis 1991, Jovanovich 1997). Starch (20 mL) was dissolved in hot 1N NaOH and then diluted to a concentration of 10 mg/mL. The solution was centrifuged at 12,000 × g for 5 min at room temperature; the supernatant was added to the top of the chromatography column. Fractions of 0.7 mL were collected (Fractometre Alpha 400 Colector, Buchler Instruments, New Jersey).

Dead and total volumes were determined using blue dextran and bromophenol blue, respectively. The anthrone-sulfuric acid method (Rose et al 1991) was used to measure the starch content of each fraction, by adding 1 mL of reagent (0.2% (w/v) anthrone, 72% (w/v) H<sub>2</sub>SO<sub>4</sub>) to 100 µL of sample. The resulting solution was heated at 100°C for 12 min, then cooled for 10 min to room temperature, and finally tested for absorbance at 625 nm, with glucose as the standard.

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### Differential Scanning Calorimetry

A calorimetry system (910, Du Pont Co., Wilmington, DE) connected to a Hewlett-Packard 7046-B recorder was used for differential scanning calorimetry (DSC). The system was calibrated with indium, and a double empty pan was used as a reference. Samples of flours and cookies were weighed in the DSC pans, and distilled water was added with a Hamilton microsyringe to obtain different water contents. The pans were then sealed and weighed to determine the exact amount of water. They remained at room temperature ( $\approx 20^\circ\text{C}$ ) for 24 hr and were then centrifuged at  $800 \times g$  for 10 min at  $20^\circ\text{C}$ , to ensure good contact between sample and pan base before DSC determinations. Samples and references were heated from 30 to  $135^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . Peak transition temperatures were determined for each endotherm. The areas of the endotherms were determined with an image analyzer (Morphomat 34 Zeiss) and converted to enthalpy using the equation:

$$\Delta H = (60A \cdot TB \cdot E \cdot \Delta qs) / m$$

where:  $\Delta H$  = enthalpy of gelatinization (J/g),  $A$  = area ( $\text{cm}^2$ ),  $TB$  = time base (min/cm),  $\Delta qs$  = sensitivity range ( $\text{J} \cdot \text{sec}^{-1} \cdot \text{cm}^{-1}$ ), and  $m$  = sample mass (g).

### Microscopy

The size and shape of triticale starch granules were studied with a microscope (Leitz-Ortholux II, Ernst Leitz Co., Wetzlar, Germany) fitted with an automatic camera (Leitz Vario-Orthomat). For each of the 10 triticale advanced lines and cultivars, photomicrographs of 250 representative starch granules in different fields were taken. The size of granules was measured and the length ranges were determined.

### X-ray Diffraction

Triticale flour or wheat starch was placed as a thin film on aluminum sample holders and analyzed with a powder diffractometer (PW 1710, Philips Argentina S.A., Capital Federal, Argentina) fitted with a crystalline graphite monochromator. The operating conditions were: Cu  $K\alpha$  radiation; voltage, 40 kV; chart speed, 10 mm/2 $\theta$ ; running rate, 2 $\theta$ /min.

### Preparation of Cookies

Cookies were prepared according to micromethod III described by Finney et al (1950) and modified at CIMMYT (1980). The ingredients used were: flour, 45.00 g; sugar, 27.00 g; vegetable fat, 20.20 g; powdered milk, 2.25 g;  $\text{NaHCO}_3$ , 0.50 g;  $\text{NaCl}$ , 0.42 g; and

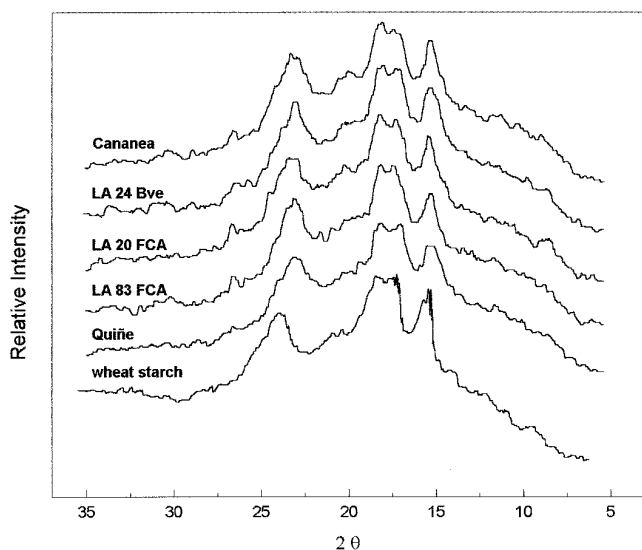


Fig. 1. X-ray diffraction patterns corresponding to flours of different experimental lines and cultivars of triticale.

water, 8.5 mL. The dough was kneaded in a spiral arm mixer (Philips HR 1495, Buenos Aires, Argentina) for 5 min. Baking was performed for 10 min at  $200 \pm 2^\circ\text{C}$  in a forced convection oven (Continental 2001, Utilidades Domésticas S.A., San Pablo, Brazil) equipped with a temperature controller.

### Water Loss During Baking

The humidity in the base, center, and surface of the cookies during baking was determined at 2, 4, 6, 8, and 10 min, by Approved Method 44-15A (AACC 1995). Analyses were performed in duplicate.

### Statistical Analysis

Each value of chemical analysis of flours represents a mean of three determinations  $\pm$  standard error. Each pair of DSC parameters ( $\Delta H$  and  $T_p$ ) was the mean of three determinations. Data were statistically analyzed by the MGLH package (SYSTAT, Evanston, IL). Significance at a level of  $P \leq 0.05$  was determined.

## RESULTS AND DISCUSSION

### Characterization of Flours

The chemical composition of flours obtained from the triticale lines and cultivars under study was discussed in previous work (Leon et al 1996). The contents of protein, starch, lipids, and water (moisture) were within the ranges (% w/w): protein,  $11.9 \pm 0.2$  to  $14.0 \pm 0.1$ ; starch,  $72.0 \pm 0.9$  to  $68.2 \pm 1.1$ ; lipids,  $1.5 \pm 0.1$  to  $1.0 \pm 0.1$ ; moisture,  $14.0 \pm 0.1$  to  $13.6 \pm 0.1$ . Each value represents a mean of three determinations  $\pm$  standard error.

### Microscopy

Two types and sizes of starch granules were observed in the flours obtained from different triticale advance lines and cultivars used in this work: large lenticular and small spherical. Lengths ranged from

TABLE I  
Advanced Lines and Cultivars of Triticale Samples

Sample	Name	Origin <sup>a</sup>
1	Cananea	CIMMYT, Mexico
2	Currency	CIMMYT, Australia
3	Eronga	CIMMYT, Mexico
4	LA 24 Bve	INTA, Argentina
5	LA 20 FCA	FCA-UNC, Argentina
6	LA 83 FCA	FCA-UNC, Argentina
7	Tatú	CIMMYT, Mexico
8	Tehuelche	INTA, Argentina
9	Quiñé	FAV-UNRC, Argentina
10	Yagan	INTA, Argentina

<sup>a</sup> CIMMYT = Centro Internacional de Mejoramiento de Maíz y Trigo, Mexico. INTA = Instituto Nacional de Tecnología Agropecuaria, Argentina. FCA-UNC = Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Argentina. FAV-UNRC = Facultad de Agronomía y Veterinaria, Universidad Nacional de Río Cuarto, Argentina.

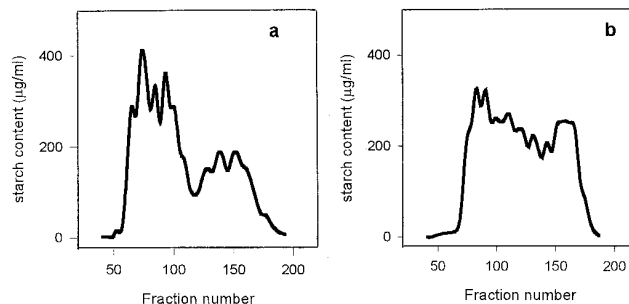


Fig. 2. Gel-permeation chromatography patterns corresponding to wheat starch (a) and the pool of triticale starch from experimental lines and cultivars under study (b).

2 to 7  $\mu\text{m}$  for the small granules and from 11.9 to 30.6  $\mu\text{m}$  for the large ones. The average length of the latter was 18.7  $\mu\text{m}$ .

By studying starch granules in three lines of triticale, Karlsson et al (1987) found a mean diameter of 16.5  $\mu\text{m}$ , the size of the larger granules being 18  $\mu\text{m}$ . These values are in agreement with those obtained in our study. Triticale starch granules are slightly larger than those of wheat and rye (Karlsson et al 1987, Hosney 1994).

The lengths of the large starch granules reported here were normally distributed ( $P \leq 0.01$ ), as indicated by the Kolmogorov-Smirnov test (Wilkinson 1990) (Nonparametric module, SYSTAT statistical package). Our normal distribution was wider than that of Karlsson et al (1987), possibly because of the larger number of cultivars used here.

### X-ray Diffraction

X-ray diffraction was used to characterize the starch of the experimental lines and cultivars of triticale studied here. Previous literature has indicated that, generally, cereal starches give A-patterns (Zobel 1988, Hosney 1994). Figure 1 shows the X-ray diffraction pattern of wheat starch and those obtained with the flours of some of the lines and cultivars tested in this work (Cananea, LA 24 Bve, LA 20 FCA, LA 83 FCA, and Quiñé). As seen in Fig. 1, A-form characteristic peaks were obtained, in agreement with results reported by other authors (Zobel 1988, Jovanovich et al 1992, Lii and Lee 1993).

Interplanar distance values ( $d$ ) of starch in most of the lines and cultivars of triticale tested here were 5.96, 5.26, 4.98, and 3.94 Å. These values were very similar to those obtained for wheat starch. Compared to diffraction diagrams of wheat starch, triticale starch diagrams showed a lower relative intensity, with slightly wider peaks (particularly in the Quiñé cultivar). Therefore, the results suggest a lower extent of starch crystallinity in the triticale lines and cultivars studied.

### Gel-Permeation Chromatography

Figure 2 shows the results obtained by gel-permeation chromatography for wheat starch and for the pool of starch obtained from the triticale lines and cultivars. The profile obtained for wheat starch may be divided into two zones: one is more intense, and corresponds to larger molecules (fractions 60–110), while the other represents smaller molecules, which are retained to a larger extent by the gel (fractions 110–185). In triticale starch, a slightly narrower and more homogeneous distribution was observed.

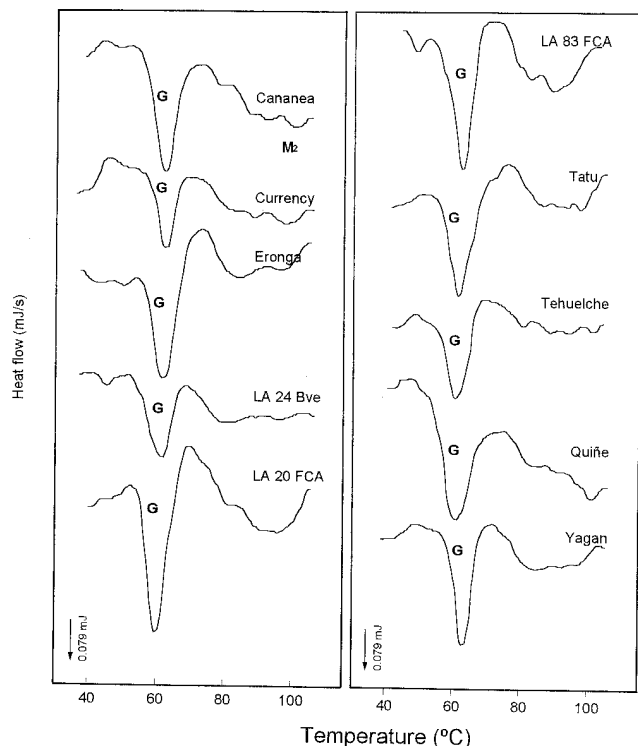
Differences in the degree of branching of starch chains also affect the degree of retention of molecules in the column matrix. A higher degree of branching means a lower degree of retention since these molecules are more compact. The shape of the molecules in solution could affect the extent of polymer-matrix interactions. The more-branched fractions result in weaker interactions and therefore in a smaller elution volume than that obtained with the linear or less-branched molecules (Bradbury and Bello 1993). Therefore, the results obtained here could indicate that triticale starch consists of chains of smaller size or a lower degree of branching than wheat starch.

### Differential Scanning Calorimetry

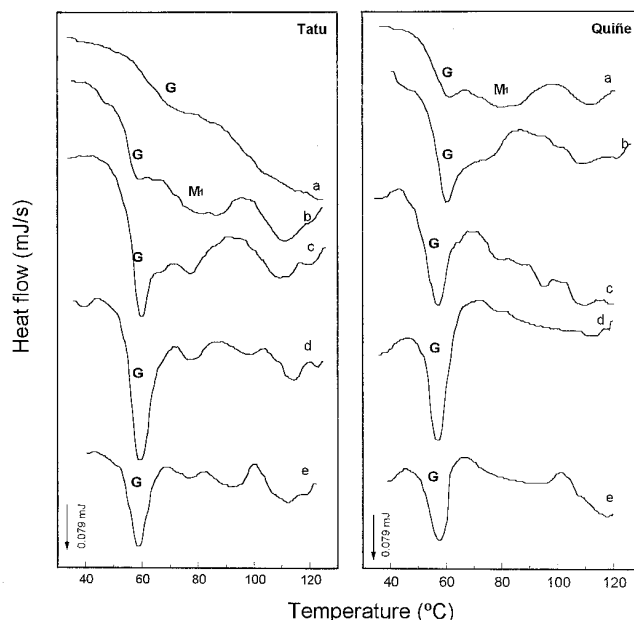
Figure 3 shows the typical thermograms obtained when heating flour of advanced lines and cultivars of triticale previously moistened to high water contents (70.6–75.7%). Only a single endothermic peak was observed (peak G), representing the gelatinization phase change. In the thermograms of some of the triticale flours analyzed, a second endotherm,  $>100^\circ\text{C}$ , was detected. This endotherm (peak  $M_2$ ) could correspond to a reversible dissociation of the amylose-lipid complex (Kugiyima et al 1980, Jovanovich et al 1992).

By using thermogram data, we calculated the enthalpy of the gelatinization process ( $\Delta H$ ) and the apparent transition temperature ( $T_p$ ) (Table II). Statistical analysis of gelatinization temperatures ( $P \leq 0.05$ ) did not give significant differences in advanced lines and cultivars except for LA20 FCA (with the lowest gelatinization temperature) and Yagan cultivar (with the highest gelatinization temperature). For enthalpies, Quiñé cultivar had the lowest value and LA 24 Bve the highest.

The mean temperature of gelatinization ( $60.4^\circ\text{C}$ ) of the 10 triticale lines and cultivars studied here is similar to that found by



**Fig. 3.** Representative differential scanning calorimetry thermograms of the flours of the advanced lines and cultivars of triticale under study at high water content (70%). G = gelatinization.  $M_2$  = amylose-lipid complex melting.



**Fig. 4.** Representative differential scanning calorimetry thermograms of Tatu and Quiñé flours at different water content: 35% (a), 45% (b), 50% (c), 65% (d),  $>70\%$  (e). G = gelatinization.  $M_1$  = melting.

Zamponi et al (1990) for wheat and slightly lower than that found for rye (Hoseney 1994).

The mean value of the gelatinization enthalpy (4.98 J/g of flour) is lower than those reported for wheat flour, 5.85 J/g (Zamponi et al 1990) and 9.3 J/g (Münzig 1991), possibly because of differences in structure between wheat and triticale starches, in DSC parameters (e.g., scanning rate, sample size), or in the method used for preparing the sample.

Figure 4 shows typical thermograms of two triticale flours (Quiñé and Tatú flours) obtained at several water contents. The gelatinization range becomes narrower as the water content increases. At  $\leq 50\%$  water content, a biphasic endotherm showing peaks G and  $M_1$  is observed. The latter peak corresponds to the fusion of the most stable crystallites (Donovan 1979, Biliaderis et al 1980). As water content decreases, endotherms G and  $M_1$  shift to higher temperatures, and the enthalpy of the G endotherm diminishes. Figure 5 shows, for decreasing water contents, an increase in the gelatinization temperature and a decrease of the gelatinization enthalpy in the flours of Quiñé and Tatú. For water contents  $>40\%$ , the gelatinization temperature of Tatú starch becomes independent of the water content during heating.

The behavior of cultivar Quiñé is different from that of the other nine triticale lines and cultivars analyzed here, requiring a higher water content ( $>60\%$ ) to complete starch gelatinization. The behavior of starch gelatinization in respect to the water content obtained for the triticale flours is similar to those reported for wheat flour and starch (Zamponi et al 1990, Munzig 1991, Biliaderis 1992)

### Changes in Cookie Starch During Baking

Triticale flours have been found to be more suitable for the manufacture of products that may be prepared with a gluten of a lower tenacity than that needed in bread manufacture (Rodgers 1973, Tsen 1974, Peña and Amaya 1980). In a previous work (Leon et al 1996), we showed that triticale could constitute a good alternative for cookie manufacture. For these reasons, we wanted to know the triticale starch behavior during the cookie baking process.

The thermal behavior of dough cookies was analyzed and compared with those observed in the baked cookies and the flour. A typical thermogram obtained for dough cookies is shown in Fig. 6. Two endotherms are seen  $>40^\circ\text{C}$ , corresponding to starch gelatinization (peak G) and the melting of the amylose-lipid complex (peak

$M_2$ ), whereas,  $<40^\circ\text{C}$ , a peak representing the melting of the vegetable fat of cookies could be seen (results not shown). Bearing in mind the amount of water used when preparing the dough cookies and the humidity of the flour (0.38 g of water/g of flour, wb), as well as the behavior observed during the thermal analysis of flour samples at low water contents (Fig. 4), one would expect two endotherms to be obtained; one for gelatinization and the other for melting of the small starch crystals. The single endotherm obtained could be attributed to the presence of sucrose in the cookie formulation. Abboud and Hoseney (1984) also reported a single endotherm in nonfat cookies prepared with wheat flour.

Solutes present in the cookie dough (sucrose and NaCl) affect the process of starch gelatinization; however, controversial results have been reported in the literature for sugar and water contents similar to those present here. Spies and Hoseney (1982), Ghiasi et al (1983), and Aboud and Hoseney (1984) indicated that starch gelatinization enthalpy increases in the presence of sugar, whereas Kim and Walker (1992) and Lim et al (1992) found that it decreases. Eliasson (1992) did not observe changes. With regard to the effect of NaCl, for salt-starch ratios similar to those of our work, Chinachoti et al (1990) observed a decrease in the enthalpy of gelatinization. At low water contents, the sugar acts in the cookie dough as a low molecular weight cosolute with starch; in this situation, the sugar is a plas-

TABLE II  
Peak Temperature ( $T_p$ ) and Enthalpy of Gelatinization ( $\Delta H$ )  
of Triticale Flours<sup>a,b</sup>

Flour	Water <sup>c</sup> (%)	$\Delta H$ (J/g)	$T_p$ ( $^\circ\text{C}$ )
Cananea	75.7 $\pm$ 3.3	4.77 $\pm$ 0.42a	60.5 $\pm$ 0.6a
Currency	72.2 $\pm$ 2.3	4.90 $\pm$ 0.17a	60.7 $\pm$ 0.7a
Eronga	72.2 $\pm$ 3.2	4.95 $\pm$ 0.13a	61.0 $\pm$ 0.6a
LA 24 Bve	74.2 $\pm$ 1.5	6.61 $\pm$ 0.25b	60.0 $\pm$ 0.4a
LA 20 FCA	72.3 $\pm$ 1.3	4.98 $\pm$ 0.08a	58.6 $\pm$ 0.8b
LA 83 FCA	72.8 $\pm$ 1.6	4.85 $\pm$ 0.25a	59.6 $\pm$ 0.3a
Tatú	74.7 $\pm$ 3.8	5.27 $\pm$ 0.17a	60.8 $\pm$ 0.2a
Tehuelche	72.2 $\pm$ 2.2	4.85 $\pm$ 0.13a	61.1 $\pm$ 0.3a
Quiñé	70.6 $\pm$ 2.3	4.10 $\pm$ 0.35c	59.9 $\pm$ 0.7a
Yagan	71.1 $\pm$ 1.1	4.52 $\pm$ 0.25a	62.1 $\pm$ 0.5c

<sup>a</sup> Mean  $\pm$  standard error ( $n \geq 3$ ).

<sup>b</sup> Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

<sup>c</sup> Water content in the differential scanning calorimetry pans.

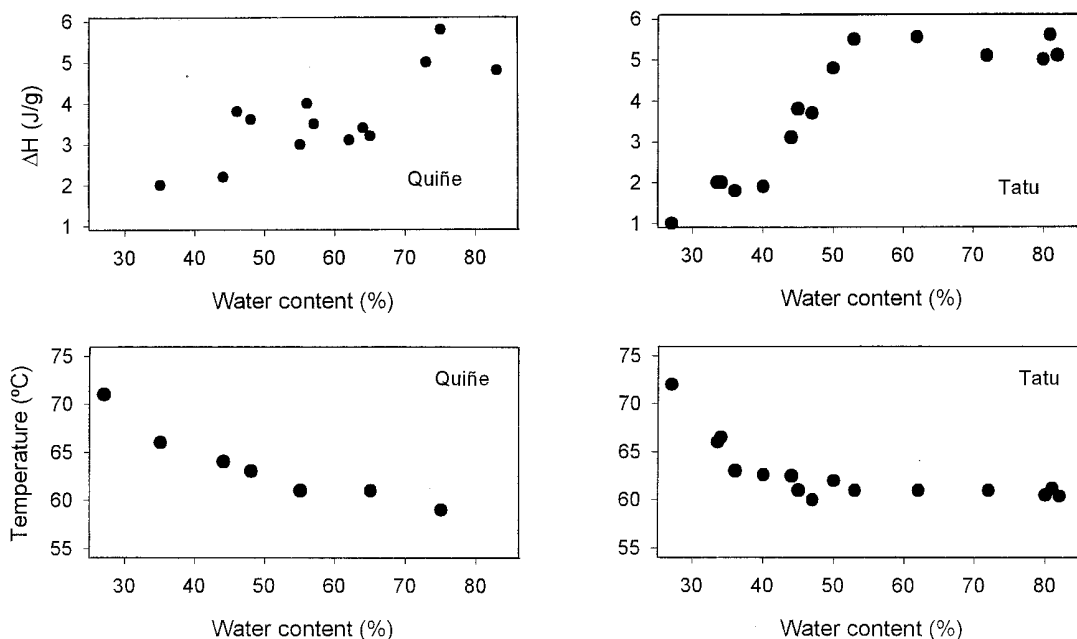


Fig. 5. Temperature and enthalpy of gelatinization of Tatú and Quiñé flours at different water contents.

**TABLE III**  
Enthalpy ( $\Delta H$ ) and Temperature of Gelatinization ( $T_g$ ) of Starch in Cookies Prepared with Different Triticale Flours<sup>a</sup>

Sample	Surface		Center		Base	
	$\Delta H$ (J/g)	$T_g$ (°C)	$\Delta H$ (J/g)	$T_g$ (°C)	$\Delta H$ (J/g)	$T_g$ (°C)
Eronga	5.48 ± 0.31 <sup>a</sup> <sup>b</sup>	64.2 ± 0.9 <sup>a</sup>	4.18 ± 0.27 <sup>a</sup>	69.2 ± 0.7 <sup>a</sup>	4.73 ± 0.16 <sup>a</sup>	61.4 ± 0.5 <sup>a</sup>
LA 24 Be	7.24 ± 0.36 <sup>b</sup>	65.5 ± 0.5 <sup>a</sup>	3.97 ± 0.14 <sup>a</sup>	67.0 ± 0.6 <sup>b</sup>	3.47 ± 0.12 <sup>b</sup>	64.9 ± 0.4 <sup>bd</sup>
LA 20 FCA	5.86 ± 0.31 <sup>a</sup>	63.0 ± 0.8 <sup>a</sup>	2.97 ± 0.24 <sup>b</sup>	67.3 ± 0.8 <sup>b</sup>	2.55 ± 0.21 <sup>c</sup>	61.2 ± 0.7 <sup>a</sup>
Tatú	6.23 ± 0.24 <sup>a</sup>	65.1 ± 0.6 <sup>a</sup>	3.39 ± 0.21 <sup>b</sup>	67.6 ± 0.3 <sup>ab</sup>	4.73 ± 0.19 <sup>a</sup>	62.8 ± 1.1 <sup>ac</sup>
Yagan	5.19 ± 0.37 <sup>a</sup>	65.4 ± 0.5 <sup>a</sup>	3.18 ± 0.17 <sup>b</sup>	67.8 ± 0.7 <sup>ab</sup>	3.26 ± 0.18 <sup>b</sup>	63.9 ± 0.9 <sup>b-d</sup>

<sup>a</sup> Mean ± standard error ( $n \geq 3$ )

<sup>b</sup> Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ )

**TABLE IV**  
Dunnet Test Results for Enthalpy ( $\Delta H$ ) and Temperature of Gelatinization ( $T_g$ )<sup>a</sup>

Treatment	$n$	$\Delta H$ (J/g)			$T_g$ (°C)		
		$X$	SE	$n$	$X$	SE	
Flour	5	5.36	0.71	5	60.26	1.58	
Base	5	3.85	1.13	5	62.82	1.58	
Center	5	3.31	0.75	5	67.79	0.85	
Surface	5	6.02	0.84	5	64.64	1.06	

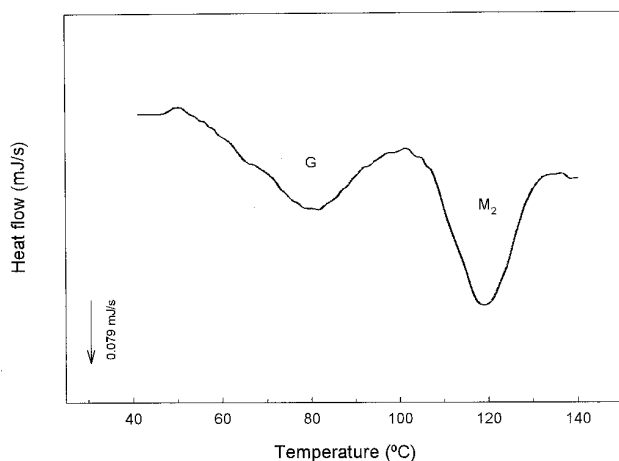
<sup>a</sup>  $X$  = mean. SE = standard error.

**TABLE V**  
Analysis<sup>a</sup> of Differences for Enthalpy ( $\Delta H$ ) and Temperature of Gelatinization ( $T_g$ )

Comparison	$\Delta H$ (J/g)	$T_g$ (°C)
Base to flour	-1.51** <sup>b</sup>	2.6**
Center to flour	-2.05**	7.5**
Surface to flour	0.66	4.4**

<sup>a</sup> Analysis of results from Table IV.

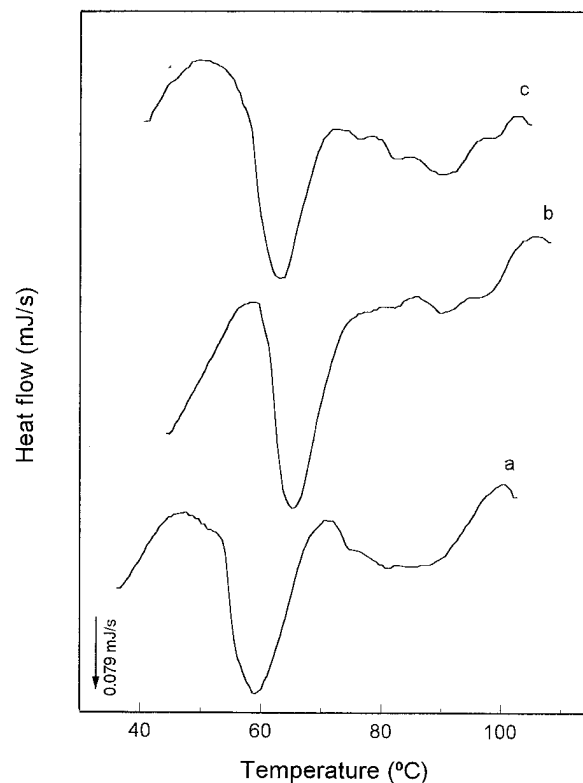
<sup>b</sup> Significant difference for  $P \leq 0.05$ .



**Fig. 6.** Representative differential scanning calorimetry thermograms of dough cookies. G = gelatinization,  $M_2$  = amylose-lipid complex melting.

ticizer of starch. By contrast, for water contents above  $W'_g$  (maximum unfreezable water), as occurred in samples taken from the center, base, and surface of baked cookies (Fig. 7), the sugar no longer behaves as a cosolute with starch, but as a plasticizing cosolvent with water. The average molecular weight of this sugar-water coplasticizer is higher than that of water alone, and it plasticizes starch less than does water alone. This effect causes an increase of the gelatinization temperature (Slade and Levine 1994).

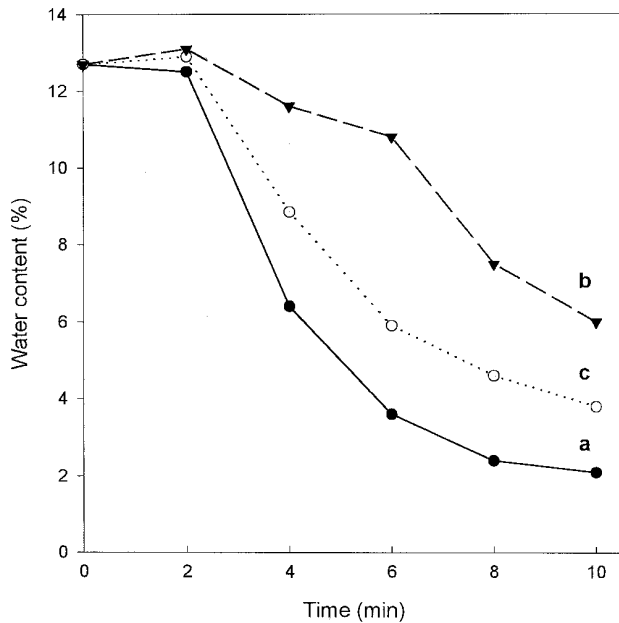
Table III shows enthalpies and gelatinization temperatures of starch in the surface, center, and base of the baked cookies prepared with



**Fig. 7.** Representative differential scanning calorimetry thermograms of the base (a), center (b), and surface (c) of cooked cookies moistened to a water content of 70%.

flours obtained from two triticale advanced lines and three cultivars, moistened to a water content of 70%, before the DSC runs. The baked cookies were analyzed in the DSC at this water content to evaluate the possible gelatinization that occurred during the cooking process (Fig. 7). The enthalpies of gelatinization were always higher on the surface of the cookies, whereas the gelatinization temperatures were lower at the base, intermediate at the surface, and higher in the cookie center. Gelatinization enthalpies and temperatures in the three zones described above were compared with the values ( $\Delta H$  and  $T_g$ ) corresponding to the flours used, both in the presence of high water contents (Table IV), using the Dunnet test (Dunnet 1964). The differences found (Table V) may be attributed to the presence and proportion of solutes in cookie dough and also to the degree of gelatinization reached by starch during baking.

In this regard, it must be considered that the degree of gelatinization obtained during cookie baking depends on the amount of water available. The formulation used includes an amount of water of  $\approx 0.5$  g/g of starch in the cookie dough. This value should be considered enough to partially gelatinize the starch (Fig. 4) (Chinachoti et al 1990). However, the presence of proteins and other ingredients in the dough may decrease the amount of water available. In addition, there is extensive water loss during baking (Fig. 8). In this sense, the



**Fig. 8.** Water loss of the base (a), center (b), and surface (c) of cookies during baking.

moisture loss is fast and significant both at the base and at the surface of the cookie, being less noticeable in its center.

Our results show that no gelatinization took place at the surface because the amount of water available is decreased by evaporation during baking, as shown by the values found for the amount of water lost (Fig. 8). In the base and center of the cookies, however, the amount of water available is enough to partially gelatinize the starch (averaging 29% at the base and 33% in the center).

Other components of cookie dough have a more important effect on the temperature of starch gelatinization than water. Several authors have reported that the addition of sugar increases the gelatinization temperature of starch obtained from different sources (Ghiasi et al 1982, Chinachoti et al 1991, Eliasson 1992, Kim and Walker 1992, Lim et al 1992) and that the presence of salt up to 2% has a similar effect (Ghiasi et al 1982, Chinachoti et al 1991, Lii and Lee 1993). From these observations we are allowed to assume that the higher temperature of gelatinization detected at the center of the cookies would result from higher concentrations of both sucrose and NaCl in this zone, the surface and the base having intermediate and lower concentrations, respectively. According to the formulation used here, the sucrose-starch ratio in cookie dough was  $\approx 1$ . Lim et al (1992) reported an increase from 60.5 to 66.0°C for a similar ratio. According to their results, the increase in the gelatinization temperature found in our study would correspond to a sucrose-starch ratio of 1 on the surface and values varying between 1 and 2 in the center of the cookie. These data suggest that water migrating from the center toward the cookie exterior during baking results in a counter-diffusion of small-sized solutes to the cookie center, thus affecting the amount of water available for starch gelatinization.

#### ACKNOWLEDGMENTS

We acknowledge financial support from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Consejo de Investigaciones de Córdoba (CONICOR), and Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba.

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[Received November 25, 1997. Accepted May 22, 1998.]