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Prediction of rice texture from starch profiles measured using high-performance liquid chromatography

Hazel Fromm
University of Arkansas, Fayetteville

J. F. Meullenet
University of Arkansas, Fayetteville

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Hazel Fromm[*] *and J.-F. Meullenet*[§]

ABSTRACT

Starch determines a large proportion of the textural properties of cooked rice. The amylose: amylopectin ratio plays a significant role in the functionality of native starch. In this study a medium-grain rice cultivar, 'Bengal', was used for starch structure characterization using high performance size-exclusion chromatography (HPSEC). This cultivar is characterized by having lower amylose content (15% to 20%) than long grain cultivars and being sticky when cooked, similar to short-grain cultivars. Rice samples were harvested in 1999 from five locations around Arkansas at state verification trials where cultural practices are closely monitored. Samples of this cultivar stored at a specified moisture level for a pre-determined period of time were also subjected to texture analysis by means of a Texture Analyzer. The data measured with the HPSEC was related to instrumental texture attributes. Chemical characterization data (carbohydrate profiles) of rice samples were used to predict texture attributes of cooked rice such as hardness and stickiness. Instrumental texture attributes of hardness and stickiness were successfully predicted for Bengal rice from starch-profile data obtained though HPSEC analyses. Both attributes proved to be well predicted, based on their high coefficients of determination of 0.97 and 0.85, respectively. The statistical analysis indicates that starch structure characterization using HPSEC may be related to instrumental measurements of texture attributes.

[*] Hazel Fromm graduated in May 2001 with a degree in food science.

[§] J.-F. Meullenet, faculty sponsor, is an assistant professor in the Department of Food Science.

Meet the Student-Author

Hazel Fromm

I graduated in May 2001 as a Senior Scholar with a major in food science and a minor in agricultural business. I transferred to the U of A in 1999 after earning a degree as an agronomist from the Zamorano Pan American School of Agriculture in Honduras. I was awarded the Foundation for the International Exchange of Students (FIES) scholarship to attend the University of Arkansas. My two years at the U of A have been an exciting learning experience, both inside and outside the classroom.

Since my arrival at the U of A, I have been able to gain practical experience in my field of study outside the classroom by working in different laboratories at the Department of Food Science. I have worked in the Sensory Laboratory, the Rheology Lab, and the Pickle Lab. Through this exposure and hands-on work, I have been able to determine which area I would like to specialize in as I advance into graduate studies. I am particularly interested in sensory science. By means of my undergraduate research I was able to acquire laboratory and research skills that will definitely prove to be useful throughout my graduate education.

My co-curricular activities include the Food Science Club, of which I served as president, member of the Institute of Food Technologists Student Association, Gamma Sigma Delta and Golden Key Honor Societies, and Bumpers College Ambassador. I had the opportunity do a summer internship abroad at the Scottish Agricultural College. I was able to carry out research related to my field of study, experienced from an international perspective.

I was an intern at Nestlé in York, England, in summer of 2001—working on textural analysis of low-calorie chocolate. Beginning in fall 2001, I will be attending graduate school at Cornell University, where I plan to specialize in dairy and sensory science.

INTRODUCTION

Starch is the principal component of rice and is made up mainly of a mixture of the polysaccharides amylose and amylopectin. Typically starches contain 20-30% amylose and 70-80% amylopectin. Starch is a polymer of glucose and an alpha-glucan containing mainly alpha 1,4-glucosidic linkages with smaller alpha 1,6-glucosidic linkages forming branch points (Pomerzanz, 1971). Starch dictates a large proportion of textural properties of cooked rice (Hamaker, 1999). The amylose: amylopectin ratio plays an important role in the functionality of native starch. Starch characteristics such as viscosity, gelatinization, and texture are functions of the amylose:amylopectin ratio (Satin, 2000). Structure of the amylose and amylopectin molecules, or their degree of polymerization, will also affect starch structure and function (Hegenbart, 1996).

Several physical characteristics of starch granules have an impact on its functionality. These characteristics include size, shape, surface, and distribution of starch granules (Satin, 2000). The organization of starch granules can be greatly influenced by genotype and environmental conditions (Smith et. al., 1997). This result can be attributed to the various isoforms of starch synthase, an enzyme responsible for the formation of amylopectin (Priess and Sivak, 1996). Starches may be altered physically, chemically, or enzymatically in order to improve functional properties (Lineback, 2000).

'Bengal'- a medium-grain rice cultivar, has lower amylose content and is sticky when cooked, similar to short-grain cultivars (Uebersaz, 2000). The amylose content of medium grain rice ranges from 15% to 20% (Webb et. al., 1979). According to Juliano et. al. (1981), variation in amylose content of milled rice is a factor that considerably affects the texture and thus the cooking and eating qualities of rice.

Investigators from the University of Arkansas Rice Processing Program have observed that the existing medium-grain cultivar, Bengal, seems to be more susceptible to variability in functionality than long-grain cultivars. For this reason, they hypothesized that not all cultivars present the same degree of susceptibility to quality inconsistency. If specific physical and chemical characteristics that are linked to high functional variability can be identified, this information could be useful to rice breeders in producing rice that is not as susceptible to functional variability as existing cultivars are.

The objectives of the study were to (1) characterize starch structure using High Performance Size-Exclusion Chromatography (HPSEC) and relate the data obtained to instrumental texture attributes, and (2) use chemical characterization data (carbohydrate profiles) of rice samples to predict texture attributes of cooked rice such as hardness and stickiness.

MATERIALS AND METHODS

Rice Samples. Bengal rice was used for this study. Rice samples were harvested in 1999 from five locations around Arkansas at state verification trials where cultural practices are closely monitored. The locations were the following: (Bengal A) Mississippi County; (Bengal B) Cross County; (Bengal C) Greene County; (Bengal D) Prairie County; and (Bengal E) Mississippi County, in the same field as BA but after a heavy rain prior to harvest (5.44 cm on 29 Sept. 1999). All locations are privately owned, with the exception of Mississippi County location, which is part of the North East Research and Extension Center (NEREC). Harvested rice was transported to the Rice Processing Laboratories at the Food Science Department, University of Arkansas, Fayetteville, where it was cleansed and dried in a laboratory drier at 33ºC and 67.8% relative humidity (low temperature drying).

The samples were then subjected to several post-harvest treatments, including assessment of equilibrium moisture content and storage duration. The rough-storage moisture contents for all 15 samples were equilibrated to 12% in an equilibrium chamber at 21ºC. Finally the samples were stored at 21ºC and sampled at 0, 12, and 24 weeks. The samples from each location were then stored in a freezer until further chemical and textural analyses were conducted. The moisture content of the samples after extended storage (approx. 16 months) ranged from 8% to 16%, depending on location and storage time. Bengal rice samples at 0 weeks had the lowest moisture content, averaging 9.5% across the five sampled locations.

Starch Isolation. Rice starch was isolated using a modified alkaline method (Hoover and Sosulski, 1985). A 0.2% NaOH solution was used to extract the starch. The dried starch cake that resulted was ground and stored at -20ºC. The isolated rice starch obtained was then used to prepare the defatted starch samples for high-performance liquid chromatograph (HPLC) injection. Defatted starch was obtained by pipetting 10 mL of butanol for every gram of rice starch. Samples were left shaking (LabQuake, Barnstead/Themolyne, Dubuque, Iowa) overnight. Samples were collected into aluminum pans and left to dry.

Starch samples for HPLC injection were prepared by adding 5 mL of 90% methylsulfoxide to 20 mg of defatted rice starch. Samples were placed in a water bath for 1 hour and stirred overnight. Finally, the samples were filtered through a 5-µm Waters brand membrane.

Instrumental Texture Analysis. Instrumental texture analysis of the samples was carried out using a Texture Analyzer (Model TAXT2i, Texture Technologies Corp., Scarsdale, N.Y.) equipped with Texture Expert data acquisition software (Version 1.22, Stable Microsystems, Surrey, England). A compression fixture (100-mm diameter compression plate) and base plate were required for the double compression test. A 50-kg load cell was used with the instrument, allowing a return distance of 30 mm.

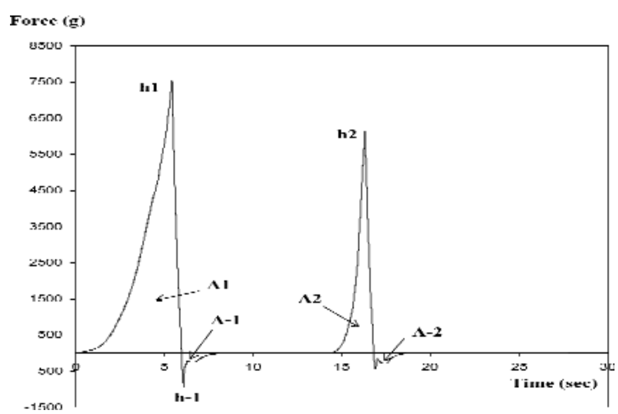
Sample preparation for instrumental texture analysis required samples to be cooked for 30 minutes in a rice cooker under steam conditions (Aroma Rice Cooker/Steamer, Model ARC-707, San Diego, California). Ten grams of milled rice were placed in a 100 ml beaker and combined with 17 g of water. Once water in the rice cooker (350 ml) was boiling, the sample was placed on a rack in the center of the cooker to prevent direct contact with the heated surface. After 30 minutes, the rice cooker was turned off and the rice remained in it for 5 minutes. Ten rice kernels were then placed on the surface of a clean aluminum base plate and analyzed. Two cooking replications were performed for each sample and six measurements were made for each cooking replication. Sample temperature was monitored closely as lower temperature instantly affects texture and would therefore produce inaccurate, unreliable measurements (Meullenet et. al., 1998, 1999).

The crosshead speed of the texture analyzer was set at 5 mm/second and the deformation to 90% of each sample's original height. A complete texture profile analysis was then obtained from the Texture Expert software. The software recorded force-distance curves for the double compression. The software was used to write and run a macro for each sample, with the purpose of calculating values for instrumental texture attributes. Calculated parameters included texture attributes such as hardness and stickiness (Fig. 1).

Starch Structure Characterization. The samples were analyzed for carbohydrate profiles by HPSEC according to methods developed by Wang and Wang (2000). Native starch was separated using a series of Shodex OHpak columns maintained at 55ºC with a column heater. Components of the HPSEC used to determine the amylose: amylopectin ratio included a 515 HPLC pump and an injector with a 100 µl sample loop, an inline degasser, and a refractive index detector. The previously mentioned equipment was used along with a high performance anion-exchange chromatograph with pulsed amperometric detection (Wang and Wang, 2000). An aqueous solution of $NaNO_3$ and NaN_3 was used as the mobile phase. Dextran polymers of various molecular weights were used as standards. The data were obtained from one replication of each rice sample.

Statistical Analyses. Chemical characterization data obtained from the HPLC analyses were used for prediction of corresponding functional attributes such as sensory texture and cooking properties. Mathematical models using multivariate analysis techniques were used to develop a predictive model (Meullenet, et al., 1999).

The statistical methods used were partial least squares regression and principal component analysis using the Partial Least Squares (PLSI) and Principal Component Analysis (PCA) options in The Unscrambler software (version 7.5, CAMO ASA, Throndheim, Norway, 1996).



Variable description	*Variable name*
Sample height at the beginning of the test	Height2
Maximum force for the first positive peak (first compression cycle)	h1
Minimum force for the first negative peak	h1
Maximum force for the second positive peak (second compression cycle)	h2
Area under the first positive peak curve	A-1
Area under the first negative peak curve	A-1
Area under the second positive peak curve	A-2
Area under the second negative peak curve	A-2
Ratio A2/A1	Cohesiveness

Fig. 1. Typical TPA test curve and instrumental parameters extracted from the force/deformation curves for TPA test.

RESULTS AND DISCUSSION

Instrumental texture attributes of hardness (h1) and stickiness (A-1) were successfully predicted for Bengal rice from starch-profile data obtained though HPSEC analyses. Both attributes proved to be well predicted as can be observed from their high coefficients of determination of 0.97 (Fig. 2) and 0.85 (Fig. 4), respectively.

The force versus time curve presented in Figure 1 was used to determine the value of the two instrumental texture parameters analyzed. Hardness can be defined as the maximum force during the first compression (H), while stickiness is the area under the first negative-peak curve (A-1).

The starch profile data were superimposed to the weighted regression coefficients for instrumental hardness (Fig. 3). As the graph shows, the first peak indicated amylopectin, which is of higher molecular weight than amylose. Since the process was one of size exclusion, this peak appeared before the amylose peak, which is a lower molecular- weight structure. The textural data indicate that higher relative concentrations of amylopectin were responsible for a lower hardness value. It was also found that an increase in low molecular-weight amylose resulted in an increase of Bengal rice hardness. Juliano et. al. (1981) found amylose content to be positively correlated with the hardness value and negatively correlated with stickiness.

Starch profile data were also superimposed on the weighted regression coefficients for instrumental stickiness (Fig. 5). In this graph, the relation between high levels of amylopectin and stickiness is positive. The peak indicating presence of the higher molecular-weight amylopectin obtained from HPSEC analysis coincides with an increase in adhesiveness. The superimposed curve of regression coefficients for stickiness begins to decline sharply at the same point at which the amylose peak begins to rise. The relationship between amylose presence and the stickiness attribute is therefore inverse.

It is relevant to point out that the HPSEC equipment used for sample analysis was not functioning at optimal conditions. This was due to deterioration of the column, and which may have caused an irregular flow of the liquid that continuously carries the sample from the top to the bottom of the column.

The statistical analysis presented indicates that starch structure characterization using HPSEC may be related to instrumental measurements of texture attrib-

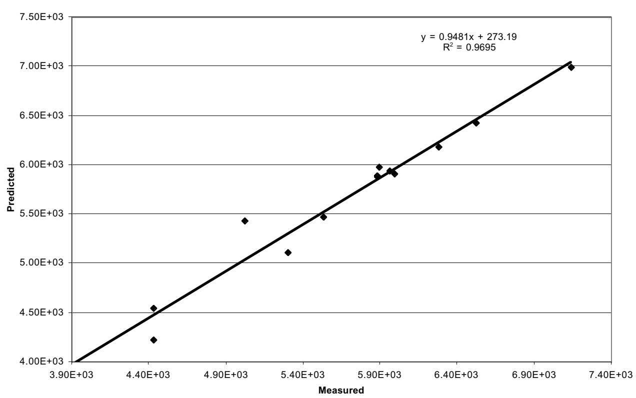


Fig. 2. Measured versus predicted hardness from HPLC data.

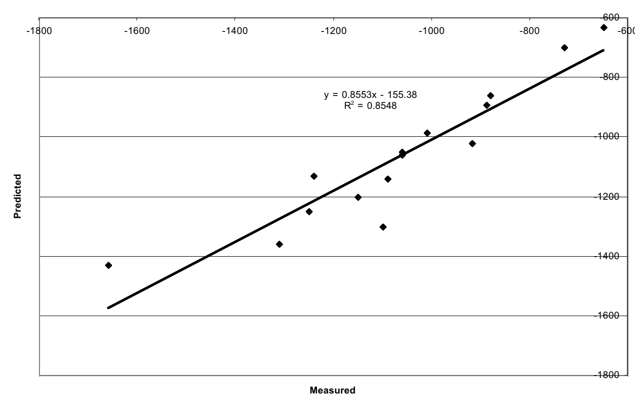


Fig. 4. Measured versus predicted stickiness from HPLC data.

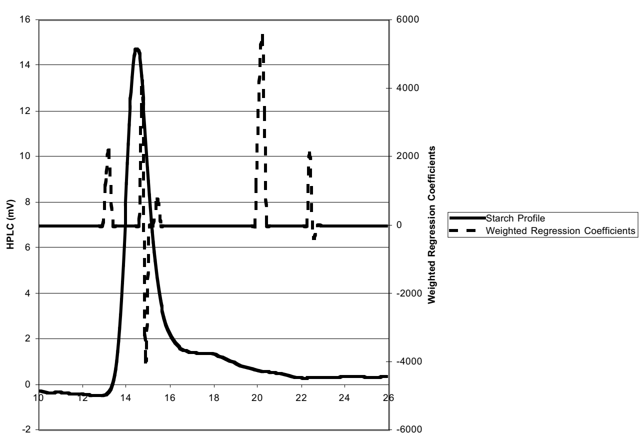


Fig. 3. Prediction of instrumental hardness (h1) from starch profile data.

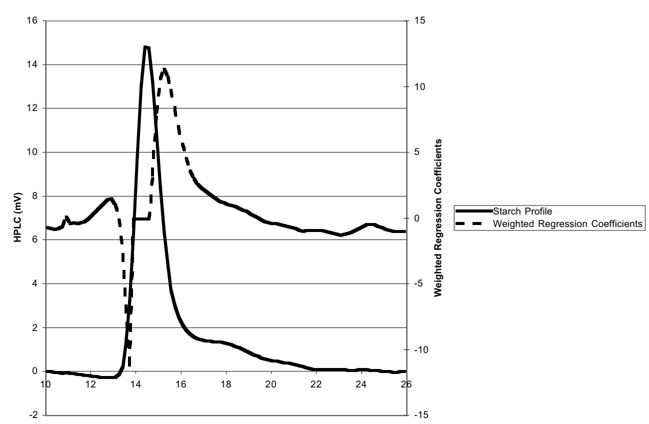


Fig. 5. Prediction of instrumental stickiness (A-1) from starch profile data.

utes. Instrumental hardness and stickiness were successfully predicted for Bengal rice from starch-profile data. Both attributes proved to be well predicted as demonstrated by their high coefficients of determination of 0.97 and 0.85, respectively. Further research is necessary to determine if these attributes can be accurately predicted for different rice cultivars based on their individual carbohydrate profile.

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