Iran Agricultural Research, Vol. 27, No. 1-2, 2008 and Vol. 28 No. 1, 2009
Printed in the Islamic Republic of Iran
Shiraz University

"Research Note"

The Physicochemical Properties of Starch Component of six Iranian Rice Cultivars

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ABSTRACT-Using a wide range of techniques, including differential scanning calorimetry, X-ray diffraction, Rapid Visco Analyser and Fourier Transform Infera Red Spectroscopy, some physicochemical properties of the starch fraction of six Iranian rice cultivars (Tarom, Tarome Hashemi, Neda, Ramezani, Fajr and Kamfirouzi) [†]were studied and compared. DSC data showed that starch granules of different rice cultivars had different gelatinization properties in terms of enthalpy, onset, peak and conclusion temperatures of gelatinization. All samples had similar X ray patterns (A type), different degrees of starch crystallinity. The rheological behaviour of rice powders during heating and the effects of heat processing were studied and compared in excess water from 25 to 95 °C. The samples were different in their pasting properties. This study indicates that starch properties should be mentioned as a crucial parameter determining the quality of rice cultivars.

Keywords: Iranian rice cultivars, Physicochemical properties, Rice, Rice starch

INTRODUCTION

Rice (*Oryza sativa* L.) belongs to the *Poceae Gramineae* or grass family and has been the human's staple food for at least 5000 years. Asian countries especially China and India are the main world producers of rice (approximately 91% of the world's rice production). This is attributed to the hot and humid climate of these countries which is well suited for rice production (8, 16). In Iran rice is mainly grown in northern parts followed by south east areas (8).

Rice provides approximately 20% of the daily calories consumed by human beings around the world. This value is much higher in Asian countries since rice is the staple food of the people of this continent and provides as much as 80% of their daily calories and 20% of their protein intake (3, 10).

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Many different products are made from rice grains or rice flour including breakfast cereals, snacks, biscuits and cakes, noodles, desserts, baby foods, beverages and rice starch. The latter is an important product used in the manufacturing of many other food and drug products (5, 13).

Milled rice consists of approximately 90% starch; therefore, its structure and physicochemical properties are the principal features used to select rice cultivars and rice starch for specific industrial applications (11, 14). Accordingly, the effects of the starch fraction of rice on the properties of the rice products have been the subject of many research projects. It is well established that starch granules of rice are the smallest amongst other cereals with the size reported to range from 3 to 8 µm. Rice granules are in the form of compounds in which many small granules (between 20 to 60 individual granules) have developed within a single amyloplast (14).

Apparent amylose content is reported to vary among rice cultivars from approximately zero in waxy rice to 30% in normal genotypes (1, 20). Rice amylose has been reported to have a degree of polymerisation and chain length ranging from 987 to 1225 and from 276 to 430 glucose units, respectively (1, 19). Rice amylopectin has an average degree of polymerisation and chain length ranging from 2700 to 1000 and from 128 to 586 glucose units, and an average chain number of 128 to 586 (1, 9). These values are affected by the genetics of the rice and its growing environment (7, 14, 22).

The swelling power and solubility of different rice cultivars are different. For instance Sodhi and Sing (2003) and Voon et al. (2009) studied five different Indian rice starches and reported that the amylose content had reverse relationship with swelling power, while having positive correlation with solubility (14, 21).

The crystalline structure of rice starch has been studied using X-ray diffraction technique. As expected, the typical A-pattern is observed for rice starch. Furthermore, it has been reported that the degree of crystallinity of rice starch is lower than other cereal starches ranging from 29.2 to 39.3 % (19, 23).

Thermal properties of normal rice starch were studied using differential scanning calorimetry (DSC) and onset (To), peak (Tp), and conclusion temperatures of 75, 82 and 87 ˚C, were reported, respectively (16). However these values are affected by rice cultivar, growth condition and sample preparation methods (12).

Pasting parameters of starch are crucial factors affecting cooking quality and gel properties, which are generally determined by Rapid Visco Analyser (RVA) or Brabender Amylograph. It has been shown that the pasting parameters of rice starch are directly correlated with amylose content (9, 26). However, there are cultivars that have similar amylose content but very different pasting properties. Pasting properties are also affected by the chain length of amylose and amylopectin, as well as environmental and post-harvest treatments (15, 17).

As important factors affecting the quality of food products, pasting, retrogradation, clarity and digestibility of rice starch have been studied in detail (6; 18).

From the literature it can be concluded that obtaining basic information on the physicochemical properties of rice is of great importance to find the right application for each cultivar. Such information is available for some rice cultivars around the world. Unfortunately, little attention has been given to rice cultivars in Iran. Therefore, the main aim of the current research was to present basic information on some physicochemical properties of rice cultivars related to their starch fraction. The results can be used for the selection of the best rice cultivars according to the quality of the final product.

MATERIALS AND METHODS

Materials

Five main Iranian rice cultivars including Tarom, Tarom-e-Hashemi, Neda, Ramezani and Fajr were kindly donated by the Northern Agricultural Research Centre of Gilan, Iran. Kamfirouzi is a well-known and favourite rice cultivar grown in Fars Province, Iran, which was obtained from Agricultural Research Centre, Zarghan, Fars, Iran. All samples were in the form of milled rice grains.

Methods

The moisture content of the grains (determined according to the approved methods of the AACC, 2000, 44-15 A) (2) was in the range of 9-11%. Samples were grounded to produce rice flour using a hammer mill, then sieved to obtain similar particle sizes in the range of 120-200 μm, used for further experiments.

Thermal properties

A differential scanning calorimetry (DSC) DSC-7 (Perkin-Elmer, Beaconsfield, UK), calibrated with indium and cyclohexane, was used to analyze modified and native starch powders. An aliquot of each powder was mixed with distilled water (starch:water, 1: 3 w/w) in a high pressure stainless steel pan and left overnight for moisture equilibrium. Each pan was scanned at a heating rate of 10 $K.min^{-1}$, from 20 to 135°C. An empty stainless steel pan was used as reference. Pyris software (Perkin-Elmer) was used to analyze the DSC traces.

X-ray diffraction pattern and degree of crystallinity

The crystalline pattern and degree of crystallinity of rice starch were studied using a wide angle X-ray Diffractometer, (APD-15 system). The degree of crystallinity was calculated as the ratio of the areas of sharp peaks to the total area of the x-ray spectrum of each sample

Pasting properties

A Rapid Visco Analyser (RVA) (Newport Scientific Pty. Ltd., Warriewood, Australia) equipped with the software Thermocline for Windows was used to study the pasting properties and to measure the apparent viscosity of the native and modified samples as a function of temperature (4).

Rice flour (3 g d.w.b.) was added to 25.0 g distilled water. The pedal blade was placed into the canister containing the sample and water and the canister was then inserted into the RVA. The stirring speed was 960 rpm for the first 10 seconds and 160 rpm for the rest of the experiment. To study the pasting profile, samples were initially held at 50 ºC for 2 min, then heated to 95 ºC at a constant rate of 0.2 ºC/s, held at that temperature for 3 minutes, and then cooled down to 50 ºC at the same rate and held for 5 minutes.

Statistical analysis

The experiments were performed in a completely randomized design. All experiments were conducted in triplicates and the mean values and standard deviations were calculated. Analysis of variance (ANOVA) was performed and results were separated using the Multiple Ranges Duncan's test ($\alpha<0.05$) using statistical software of SPSS 13 (SPSS, Inc. New Jersey, USA).

RESULTS AND DISCUSSION

Determination of thermal properties of the samples

Fig. 1 presents the DSC traces of rice powders in excess water. The endothermic peaks seen at the temperature range from 63 to 94 ˚C are indications of starch gelatinization and the conversion of semi-crystalline starch to an amorphous state as a result of gelatinization. Analysis of the DSC traces (Table 1), shows that the studied rice samples were different in terms of gelatinization temperature (GT), Kamfirouzi had the lowest, and Neda had the highest gelatinisation onset (To) (63.7 ˚C and 80.84 ˚C, respectively). Other samples had To values with no significant difference with each other (about 80 ˚C). This may indicate that during the cooking of Kamfirouzi rice, starch granules gelatinized at a lower temperature as compared to other samples. The peak temperature (Tp) of Kamfirouzi was the lowest, while Neda and Ramezani had the highest values (72.6 and 87.6 ˚C, respectively). Conclusion temperature (Tp) of Kamfirouzi was the lowest, while Ramezani had the highest value (84.73 and 94.02 ˚C, respectively). This may indicate that Ramezani required higher temperature for the full gelatinization of starch. The results also showed that Kamfirouzi had the highest gelatinization energy (11.61 J/g), while Neda had the lowest value (9.97 J/g). These results may show that the internal structures of starch granules of these rice cultivars were significantly different in terms of crystallinity and amylose and amylopectin structure.

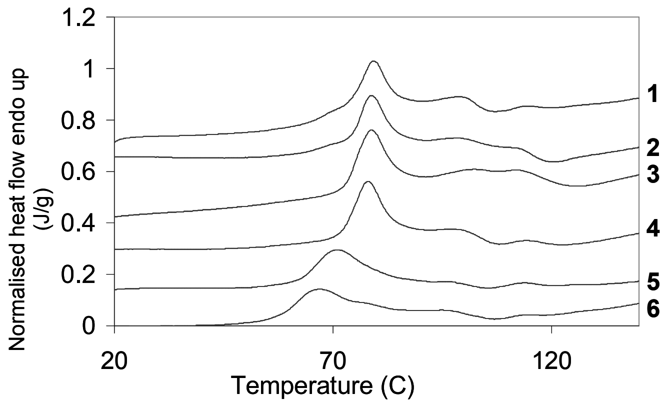

Fig. 1. DSC traces of the starch component of different rice powders determined by DSC. 1: Neda, 2: Ramezani, 3: Tarom Heshmati, 4: Tarom, 5: Fajr, 6: Kamfirouzi

X-ray diffraction pattern

The X-ray diffraction patterns of different cultivars of rice revealed an “A-pattern”, typical of native rice starch (Copeland et al. 2009; Bao and Bergman 2004) with peaks at 15, 16, 18 and 23° (Fig. 2). The degree of crystallinity of different rice cultivars varied from 15.1 to 17.7%. Fajr had the lowest degree of crystallinity (15.1%) and Neda had the highest value (17.7%). This may indicate that the crystalline structure of amylopectin molecules in the starch fraction of different rice cultivars was different. In the samples with a lower degree of crystallinity, the structure of amylopectin may be more amorphous.

Table 1. Thermal properties of the starch component of different rice powders determined by DSC*.

Rice cultivars	ΔH (J/g)	To (˚C)	Tp (˚C)	Tc (˚C)
Fajr	10.94 ± 0.68	68.07 ± 0.21	77.82 ± 0.13	89.62 ± 0.45
Kamfirouzi	11.61 ± 0.57	63.70 ± 0.33	72.60 ± 1.04	84.73 ± 2.09
Neda	9.97 ± 0.38	80.84 ± 0.13	87.17 ± 0.13	93.59 ± 0.32
Ramezani	10.07 ± 1.27	81.48 ± 0.35	87.27 ± 0.78	94.02 ± 0.93
Tarom Heshmati	10.19 ± 0.31	80.45 ± 0.33	86.53 ± 0.00	93.62 ± 0.09
Tarom	11.21 ± 0.16	79.15 ± 0.13	86.35 ± 0.78	92.75 ± 0.16

***ΔH = gelatinization enthalpy, T0 = onset temperature, Tp= peak temperature, Tc= conclusion temperature. Each value represents the mean ± Standard deviation**

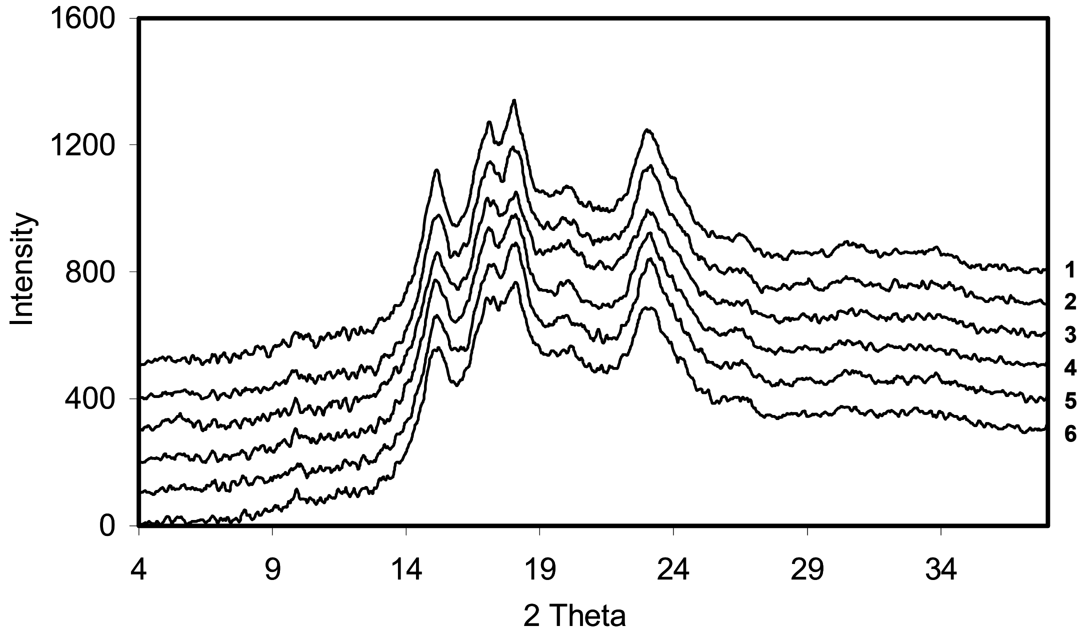

Fig. 2. X-ray diffraction spectra of the starch component of different rice powders. 1: Tarom Heshmati, 2: Neda, 3: Kamfirouzi, 4: Ramezani, 5: Tarom, 6: Fajr

Fourier Transform Infra Red (FTIR) results

The FTIR was used to look at the level of short range order in the starch granules of the samples. As Fig. 3, shows, the signal ratio at wave number of 1047/1020 was similar in all 6 samples studied. This ratio is an indication of the level of crystallinity of amylopectin in the semi-crystalline structure of starch granules.

Pasting properties of the samples

The results (Table 2) showed that the six samples were different in terms of pasting properties. Based on the RVA time-temperature profile, peak viscosity occurs at 95 ºC, at which a majority of starch granules were fully gelatinized. Increasing the viscosity of starch at this stage is a result of granular swelling and leaching of starch molecules (mainly amylose) from the granules (7). It has been shown that different starch types have different values for peak viscosity since the molecular structure of starch is different (9, 11). It is generally accepted that larger molecules can produce higher viscosity. Accordingly, the peak viscosity values obtained for different rice samples in this study were different. Tarom and Neda had the lowest and highest peak viscosities, respectively.

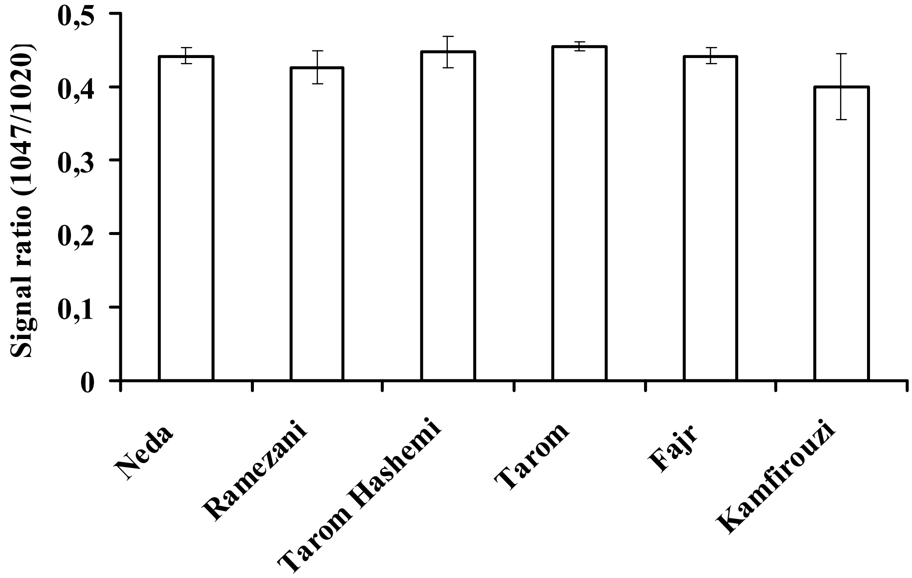

Fig. 3. FTIR of the starch component of different milled rice. A ratio of 1047/10120 is an indication of crystallinity. Each value represents the mean ± standard deviation

Table 2. Pasting properties of the starch component of different rice powders determined by RVA*.

Rice cultivars	Peak viscosity (cP)[1]	Breakdown (cP)	Final viscosity (cP)	Peak time (s)
Fajr	7306.5 ± 140.5	4271.0 ± 147.9	8011.5 ± 122.3	328 ± 20.3
Kamfirouzi	6861.0 ± 241.8	5183.0 ± 159.2	8336.0 ± 133.1	340 ± 31.7
Tarom	6422.0 ± 216.4	3791.5 ± 81.3	6855.0 ± 95.7	332 ± 30.0
Neda	7965.0 ± 67.9	4609.0 ± 108.9	8369.5 ± 65.8	384 ± 25.4
Ramezani	7297.0 ± 138.0	4267.5 ± 75.7	8223.0 ± 22.4	332 ± 33.7
Tarom Heshmati	6860.5 ± 84.1	4320.0 ± 95.4	7395.0 ± 22.3	340 ± 22.4

*** Each Value represents the mean ± Standard deviation**

[1]cP= centi Poise

Peak time, the time required to reach peak viscosity, may be affected by the packaging of starch molecules inside the granules as well as the molecular structure of starch (23, 24). Fajr, for instance, had the lowest degree of crystallinity (15.1% as determined by X-ray diffraction) and the shortest peak time. Neda, on the other hand, had the highest degree of crystallinity (17.7%) and also the highest peak time.

Breakdown viscosity was the highest for Kamfirouzi, while it was the lowest for Tarom. Final viscosity was the highest for Kamfirouzi and Neda, while it was the lowest for Tarom. This value may show the different retrogradation behaviour of rice starches. On the other hand, Tarom rice remained softer after cooling of the cooked rice while Neda became the hardest after cooling.

CONCLUSION

Broad endothermic gelatinization peaks were found on DSC traces from 45 to 125 ºC and the different rice cultivars studied showed different gelatinization behaviours. Peak temperatures of gelatinization had a wide range from 65 to 80 ºC (Kamfiruzi lowest and Neda highest). The powders also had different rheological behaviours in the RVA. The crystallinity level from X-ray and FTIR were significantly different for the examined cultivars. These findings have implications for a better understanding of the different rice varieties and their starches in food processes and their behaviour when heating. The results of this study may indicate that amongst the rice samples tested, Neda can be used to make parboiled or quick cooked rice. Moreover, to make different products from rice, such as cooked rice or breakfast cereals, Kamfirouzi is the best, since it has the fastest cooking time, and the lowest gelatinisation temperature as compared to others. Starch modification should also be done based on starch properties which are affected by the source of starch. For example, Neda, with the highest degree of crystallinity, may not be suitable for some modifications such as enzyme or acid hydrolysis. Finally, it may be concluded that to obtain high quality rice products, selection of the type of rice is of great importance. This should be done based on scientific information rather than just availability or low price of the product. Further research is required to characterise other rice cultivars in Iran based on their components as well as obtaining other physicochemical information.

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خصوصیات فیزیکوشیمیایی نشاسته برخی ارقام برنج ایرانی

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چکیده–برخی خصوصیات فیزیکوشیمیایی نشاسته موجود در شش واریته برنج ایران (طارم، طارم حشمتی، ندا، رمضانی، فجر و کامفیروزی) توسط تکنیک های مختلفی شامل گرماسنجی پویشی افتراقی، پراش اشعه ایکس ، ویسکوآنالیزر سریع، طیف سنجی به روش تبدیل فوریرمادون قرمزمورد مطالعه و مقایسه قرار گرفت. نتایج گرماسنجی پویشی افتراقی نشان داد نشاسته موجود در واریته های مختلف برنج دارای خواص ژلاتینه شدن از نظر انتالپی ، دمای ژلاتینه شدن شروع ، اوج و انتهایی بودند. تمامی نمونه ها دارای یک الگوی پراش اشعه ایکس بودند ، در حالی که درجه کریستالی بودن آنها متفاوت بود. خواص رئولوژیکی نمونه های پودر شده انواع برنج در حین حرارت دیدن از دمای۲۵تا۹۵^{o}C در آب مطالعه شد. نتایج نشان داد که نمونه های مختلف برنج خواص خمیری شدن متفاوتی داشتند. نتایج این تحقیق نشان داد که بررسی خواص نشاسته در برنج بایستی به عنوان یک عامل مهم در کیفیت آن مورد توجه قرار گیرد.

واژه های کلیدی: برنج، خواص فیزیکوشیمیایی، نشاسته برنج، واریته های برنج ایرانی

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*به ترتیب استادیار واستادیار

**مکاتبه کننده