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Thermal and cooking properties of Indian medicinal rice Njavara in aqueous and milk media

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ABSTRACT

Njavara is a medicinal red rice variety, is cooked with milk, dipped in herb extracts and topically massaged on the patient during panchakarma treatment. Pasting and thermal properties of dehusked Njavara rice flour in water and milk media were assessed and compared with two non-medicinal rice varieties PTB 39 (Jyothi) and IR 64. Solubility, swelling and X-ray diffraction pattern of Njavara rice flour were also analysed. Njavara showed high values for viscographic parameters in aqueous medium but least in milk medium, distinctive from the non-medicinal varieties. Thermal studies showed intermittent values of onset temperature (To), peak temperature (Tp) and enthalpy (ΔH) in both aqueous and milk media for Njavara. However, the gelatinization range (R) was more for Njavara. X-ray diffraction studies too showed intermittent crystallinity. The results showed that Njavara starch granules appear to be more compact at cooking temperature (98° C) compared to non-medicinal varieties and its high gelatinization range may facilitate the transfer of medicinal herb extracts to the body during topical massaging of Njavara treatment.

Keywords: *Njavara, medicinal rice, amylography, differential scanning calorimetry, X-ray crystallography*

INTRODUCTION

Rice (*Oryza sativa* L.) belongs to the Poaceae or grass family. Rice was believed to have been first cultivated in China around 6,000 years ago, but recent archaeological discoveries have found primitive rice seeds and ancient farm tools dating back about 9,000 years. The majority of the world's rice is grown in Asia, where it plays an incredibly important role in food culture.

Rice is the major source of carbohydrate mainly in the form of starch and constitutes 90% in milled rice. Brown rice has less starch compared to milled rice but the physiochemical characters like pasting, rheological and thermal are related to rice starches. Physiochemical properties of rice starch varies with variation in granule size, shape, presence of phosphate esters, relative proportion of amylose and amylopectin, their chain length distribution and occurrence and spacing of branched points in amylopectin molecule (Gunaratne and Hoover, 2002; Jane et al., 1999; Lu et al., 1997).

Njavara is a medicinal red rice variety endemic to Kerala, India. Njavara is similar to ordinary rice with husk colour varying from golden yellow to brownish black, depending upon the soil conditions (Menon, 2004). Njavara is believed to be bestowed with many medicinal properties to alleviate arthritis, cervical spondylitis, muscle wasting, skin diseases and certain neurological problems. It is a principal component in Njavara *kizhi* and Njavara *theppu*, a specialized Ayurvedic therapy for treatment of paralysis, arthritis and neurological problems.

Herein, dehusked Njavara is cooked in milk in copper vessels and the bolus tied in a muslin cloth is dipped in semi hot medicinal herb extracts such as *Sida rectusa*, *Alpinia galanga*, Triphala- a herbal formulation containing dried fruit powder of *Terminalia chebula*, *Emblica officinalis* and *Terminalia bellerica* and massaged on the body for about 30 min for about 5-7 days, depending upon the ailment. The temperature of the poultice is maintained between 60-70 °C by dipping in the warm herb extract. This treatment leads to extensive perspiration and cooling of the body and also makes the body supple, increases blood circulation and relieves stiffness from joint pains.

However, there has been no scientific data to substantiate the medicinal properties of Njavara. The study showed Njavara to be a good source of protein, vitamins, especially thiamine, and minerals (Deepa *et al.,* 2008). The pasting and thermal properties of Njavara in aqueous media have been recently reported (Simi and Abraham, 2008). Taking into account the method of '*kizhi'* preparation and lack of experimental data to substantiate the claims we undertook experiments on swelling, solubility properties and changes in viscosity while heating, cooking and cooling and thermal properties of Njavara brown rice in water and milk media and compared with non-medicinal rice varieties PTB 39 (Jyothi) and IR 64. Jyothi is a bold red rice variety, used in Kerala as staple rice after parboiling, while IR 64 is an un-pigmented ordinary staple rice variety. This could provide some valuable information on the use of Njavara in *kizhi/ theppu.*

MATERIALS AND METHODS

Njavara paddy was brought from Padma Ayurveda, Mannar (Kerala) while Jyothi and IR 64 paddy were procured from Agriculture Products Marketing Cooperative (AMPC) market in Bandipalya, Mysore, and Karnataka, India. Generally Njavara rice is used for the medicinal purpose after storing at room temperature, for about one year. Hence, paddy harvested in December 2003 was obtained and stored at room temperature for one year and five months and then shifted to cold (4 - 6° C) until use. All chemicals used were of Analytical Grade (Merck) unless stated otherwise. Standard potato amylose was obtained from ICN Bio medicals, Ohio, USA.

The paddy samples were dehusked using rubber roller dehusker or sheller (Satake Corporation, Tokyo, Japan) and ground into flour using a rice mill (Surabhi, India), passed through 60 mesh sieve and pass through of this sieve was taken for all the studies. The moisture content of the rice flour was determined after drying at 105° C until a constant weight was attained (Indudhara Swamy *et al.,* 1971).

Amylose of defatted brown rice flour was estimated as per the method of Sowbhagya and Bhattacharya (1979). The rice flour was defatted using 85% methanol in Soxhlet apparatus for 18-20 hours. The defatted flour was dried at room temperature to equilibrate moisture content (12- 13 %) and then stored at 4 °C, until used for amylose estimation. Total amylose equivalent, hot-water soluble amylose and from this insoluble amylose equivalent were derived. The micro-Kjeldahl method was employed to determine the total nitrogen and the crude protein (N x 5.95) AOAC (2000). The crude lipids were extracted using hexane by Soxhlet apparatus and ash contents were determined based on methods outlined in AOAC (2000).

Swelling power and solubility of brown rice flour of Njavara, Jyothi and IR 64 were determined at temperature 50 ºC to 98 ºC (boiling point of water at Mysore, 750m altitude), according to the modified method of Unnikrishnan and Bhattacharya (1981). Samples of brown rice (500 mg, d.b) were heated in about 20 ml distilled water at the above mentioned temps for 30 min with intermittent stirring. Weight of each sample was adjusted to 25 mg on cooling to room temperature and centrifuged at 3000 rpm for 45 min. The supernatant was decanted and the residue was weighed for swelling power determination. Ten ml of the supernatant was pipetted into pre-weighed petri-dishes, evaporated to dryness on water bath, dried at 135 ºC for 15 min, cooled and weighed. Swelling power and solubility of the flour was determined using the formula:

Swelling Power (SP) = Wt. of wet residue in mg / (500- wt. of the dried sample in mg)

Solubility = Wt. of dry residue in mg x 2.5 x 100 / wt. of the sample in mg (db).

Amylography was carried out in a Brabender Viscograph Type 801202 (Duisburg, FRG) fitted with a 700 cmg sensitivity cartridge as per the method of Halick and Kelly (1959). Experiments were carried out in aqueous and milk media independently in triplicates. Brown rice flour (10 %), dry basis, was slurred in water / milk in Braun mixie and made up to 500 ml. The slurry was poured into Brabender Viscograph bowl and heated at the rate of 1.5 °C per minute at an rpm of 75. The Brabender thermo regulator was set at 30 °C, at the beginning of the experiment. The slurry was heated to 95 C, maintained at 95 °C for 20 minutes and then cooled to 30 °C at the same rate, as mentioned above. The changes in viscosity (Brabender curves) occurring in the slurry were recorded on the viscograms attached to the instrument. The viscosity was measured in Brabender units (BU). Suppression weights were used when viscosity exceeded 950 BU. Viscosity (BU) was plotted against temperature (ºC).

The Brabender amylograms were read to give the following parameters- Peak Viscosity (PV), Hot Paste Viscosity (HPV) and Cold paste viscosity (CPV). Parameters like Break down (BD): difference between Peak Viscosity and Hot Paste Viscosity; Set back (SB): difference between Cold paste viscosity and Peak Viscosity; Total Set back: difference between Cold paste viscosity and Hot Paste Viscosity and Relative Breakdown: ratio of break down to total set back was derived. The values shown in the Table, are the average values of three original parameters (PV, HPV and CPV) and derived parameters (BD, SB, TSB and BD_r).

DSC (Mettler Toledo, USA) was employed to conduct the thermal analysis of brown rice flour. Samples with glass distilled water/milk (1: 2) were hermetically sealed in DSC pans and equilibrated for one hour at room temperature. The samples were heated at 10° C/min over a temperature range of 25° C to 110° C, using empty pan as reference. Equipment was calibrated using indium as the reference material.

Crystallinity of brown rice flour was measured by an X-ray diffractometer (PANalytical X'Pert Pro). Samples were packed into aluminum cells and were exposed to X-ray beams (Cu-Ka wavelength, 1.5406 Å) with the generator running at 40KV and 30 mA. The total diffraction intensity was measured over the angular range 5° to 30° 2θ. Other conditions include: step size 0.017°, scan rate 2sec /step, Sollet and divergence slit 1°, receiving slit 1°, and scattering slit 0.5°. The degree of crystallinity was quantitatively estimated using the method of Nara and Komiya (1983).

Analysis of variance (ANOVA) was performed for using SPSS system for windows version 7.5. Duncan's multiple range tests (DMRT) was conducted for comparison of means, to identify significantly different means at $P < 0.05$.

RESULTS AND DISCUSSION

The total amylose, protein and lipid content of the brown rice flour samples are presented in Table 1. Moisture content varied from 13 to 13.6% wet basis. Apparent amylose (AAC) and lipid content in Njavara, Jyothi and IR 64 did not show significant difference. Protein content in Njavara was observed to be higher by 1.5 % than the two non medicinal varieties. Similar values for amylose and protein content have been reported for IR 64 (Bhat Upadya *et al.,* 2008).

Table 1. Composition of dehusked rice of Njavara and non-medicinal rice varieties

Rice variety	Moisture % (wet weight basis)	Total Amylose (dry weight basis)	Protein (%) (Nx5.95)	Lipid (%)
Njavara	13.1[a]	22.70[a]	9.52[a]	2.48[a]
Jyothi	13.0[a]	22.85[a]	7.97[b]	2.60[a]
IR64	13.6[a]	24.25[a]	7.95[b]	2.06[a]

Different letters within each column indicate mean values are significantly differently at $P < 0.05$; n=5.

Starch granules when heated with excess of water lose their granular structure and get irreversibly disrupted. This phenomenon is termed as gelatinization. Starch gelatinization is of great importance in food processing operations. Various methods like microscopic studies of granule swelling and loss of birefringence, light transmittance, viscosity studies and Differential scanning calorimetry (DSC) have been used to investigate starch gelatinization.

Swelling and solubility properties of brown rice flour of three varieties of rice over a temperature range of 50°C to 98°C (bp of water in Mysore; altitude 750 m) is represented in Table 2. The swelling power and solubility of all the samples increased with temperature as expected with Jyothi showing the highest values throughout the temperature range 50°C to 98°C. At

Table 2. Swelling Power and Solubility of Njavara, Jyothi and IR64 at various temperatures.

Temperature	Parameters	Njavara	Jyothi	IR 64
50 °C	Swelling Power	3.4[b]	4.0[a]	3.4[b]
	Percent Solubility	4.8[a]	5.8[a]	5.2[a]
60 °C	Swelling Power	4.3[a]	4.3[a]	3.8[b]
	Percent Solubility	4.8[b]	5.6[a]	4.5[b]
70 °C	Swelling Power	6.2[b]	8.1[a]	4.6[c]
	Percent Solubility	7.7[a]	7.8[a]	4.7[b]
80 °C	Swelling Power	8.3[b]	9.7[a]	7.5[c]
	Percent Solubility	4.7[b]	5.7[a]	3.9[b]
90 °C	Swelling Power	9.2[a,b]	9.9[a]	8.7[b]
	Percent Solubility	6.1[b]	8.2[a]	6.3[b]
98 °C	Swelling Power	11.8[a]	13.0[a]	13.1[a]
	Percent Solubility	8.4[c]	15.0[a]	10.2[b]

Different letters within each column indicate mean values are significantly differently at $P < 0.05$, n=3.

60°C the swelling power of pigmented rice, Njavara and Jyothi was observed to be same (4.3). Near gelatinization temperature (70°C), Jyothi showed the highest swelling power followed by Njavara. Solubility too increased in Njavara and Jyothi by 2-3 % at this temperature while in IR 64 not much change was observed. The swelling power and solubility of Njavara was found to be higher than IR 64 at the range 50 C to 80°C. At 80°C and 90°C, the swelling pattern was observed to be similar in all the three varieties. A drastic decrease in solubility was observed at 80°C all the three varieties - Njavara (39 %), Jyothi (27%) and IR 64 (17%). At 98 °C the swelling power of all three varieties was not significantly different. However, solubility increased by 83% in Jyothi, 62 % in IR 64 and 38 % in Njavara at this temperature.

The swelling power of starch has been reported to depend on water holding capacity of starch molecules by hydrogen bonding (Lee and Osman, 1991) and depends on the amylose content. When starch is heated in excess water, their crystalline structure is disrupted. The water molecules get linked, by hydrogen bonding, to the exposed hydroxyl groups of amylose and amylopectin, which cause an increase in granule swelling and solubility (Singh *et al.,* 2003). The granules become increasingly susceptible to shear disintegration as they swell, and they release soluble material as they disintegrate. Solubility is the leach out of linear molecules of amylose or linear portions of long branched chains of amylopectin at and above gelatinization temperature. The high swelling power and solubility observed in Jyothi indicate the higher susceptibility of its starch granules to disintegrate than that medicinal rice Njavara and IR 64, leading to leaching of linear molecules. Excessive leaching of starch of Jyothi may also be attributed to shorter average amylopectin chains length (Mizukami et al., 1999). The low swelling power and solubility of IR 64 suggest the presence of stronger bonding forces within the interiors of the starch granules and more amylose-lipid complex (Tester and Morrison, 1990), respectively, compared to the two pigmented rice varieties. Ong and Blanshard (1995) inferred that long chains of amylopectin interact with amylose to form double helix structures that lower the swelling and leaching of materials on cooking. This may also be responsible for low solubility and swelling of Njavara and IR 64. At boiling temperature, the swelling power is similar indicating the highest possible swelling power of the starch granules.

The parameters measured in visco-amylogram using Njavara, Jyothi and IR 64, in aqueous and milk media have been summarized in Table 3.

Njavara, Jyothi and IR 64 had almost identical amylose content (AAC) but showed difference in their pasting properties (Table 3 and Fig. 1). Pasting properties of rice starches at various concentrations (6%, 8%, 10%, 11%, 12% and 20%) have been reported by various authors (Vandeputte *et al.,* 2003; Perez and Juliano, 1979). Perez and Juliano (1979**)** suggest use of 10% slurry to differentiate high amylose content rice

Table 3. Comparison of the mean values of pasting and thermal properties of brown rice flour in aqueous and milk media

Variety	Thermal Properties				Pasting Properties							
	T_0 (ºC)	Tp (ºC)	Tc (ºC)	ΔH (J/g)	GT (ºC)	PV (BU)	HPV (BU)	CPV (BU)	BD (BU)	SB	TSB	BD_r
Njavara												
Aqueous	64^{b}	70^{b}	77^{b}	4.3^{b}	70^{a}	840^{a}	670^{a}	1725^{a}	170^{a}	885^{a}	1055^{a}	0.16
Milk	68^{b}	73^{b}	79^{b}	3.9^{c}	69^{b}	610^{b}	540^{b}	1520^{b}	90^{b}	910^{b}	1070	0.05
Jyothi												
Aqueous	60^{c}	66^{c}	72^{c}	4.0^{c}	66^{b}	500^{c}	430^{b}	1140^{b}	70^{b}	640^{b}	710^{b}	0.10
Milk	63^{c}	68^{c}	75^{c}	4.3^{b}	65^{c}	630^{b}	$597^{a,b}$	1783^{b}	60^{b}	1153^{b}	1355	0.03
IR64												
Aqueous	69^{a}	75^{a}	81^{a}	4.7^{a}	71^{a}	653^{b}	443^{b}	1270^{b}	210^{a}	616^{b}	$826^{a,b}$	0.25
Milk	72^{a}	78^{a}	84^{a}	4.8^{a}	79^{a}	885^{a}	690^{b}	2545^{a}	195^{a}	1810^{a}	1255	0.10

To initiation temperature, Tp Peak temperature, Tc Conclusion temperature, ΔH Enthalpy, GT gelatinization temperature, PV peak viscosity, CPV cold paste viscosity, BD breakdown viscosity, SB setback viscosity, TSB total setback, BDr relative breakdown. Different letters within each column indicate mean values are significantly differently at $P < 0.05$; n=3.

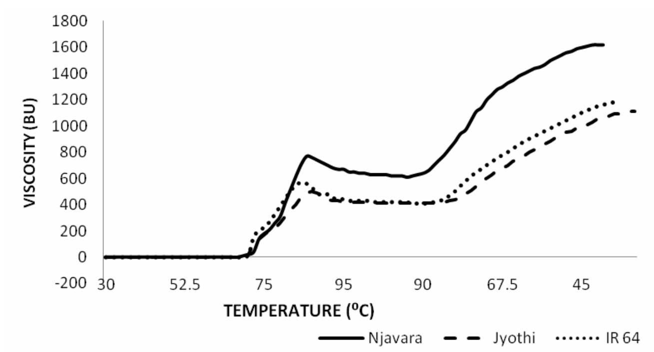

Fig. 1. Viscograms of dehusked rice of Njavara, Jyothi and brown rice of IR 64 in aqueous media

differing in gel consistency and hardness and 11-12% concentration to distinguish among intermediate and high amylose content rice varieties. The pasting temperature of Njavara (pigmented) and IR 64 (non pigmented) (~70ºC) was higher than that of Jyothi (66ºC). At this temperature, excessive swelling of the starch granules occurs, leading to disruption of the internal crystalline structure. Lower the pasting temperature faster the swelling of the starch granules as observed in case of Jyothi (Table 2 and 3). Rice flour at concentration of 20 % has been observed to be optimum for measurement of gelatinization temperature values (Halick *et al.*, 1960). According to the reports of Juliano *et al.* (1985) rice with intermediate amylose content at 10% rice flour slurry gives pasting temperatures 3 °C higher than the actual pasting temperature (20% slurry concentration), with 700g cm cartridge. Based on above reports, in the present study, the gelatinization temperature values of Njavara, Jyothi and IR 64 can be interpreted as 67 ^{0}C, 63^{0}C and 68 ^{0}C respectively. According to Vandeputte *et al.* (2003), the longer chains of amylopectin form double helices within the crystalline lamellae of starch granules thereby increasing the gelatinization temperature. Thus higher gelatinization temperature of Njavara and IR 64 may be attributed to the higher proportion of long chains of amylopectin.

Peak viscosity is the highest viscosity registered while heating the slurry up to 95° C. Increase in viscosity during the heating phase is due to swelling of starch granules as well as leaching of starch granular constituents mainly amylose. Peak viscosity in other words is the equilibrium point between swelling and leaching of starch constituents. It also reflects the fragility/rigidity of swollen starch granules in the flour against mechanical disintegration due to stirring. Among the three rice varieties studied, medicinal rice showed highest peak viscosity of 840 BU followed by IR 64 showing approximately 653 BU and least by Jyothi, 500 BU. This showed the fragile nature of starch granules of Njavara compared to those of IR 64 and Jyothi. Peak viscosity is believed to be correlated to amylopectin and amylose chain length. Longer amylopectin chains increase peak viscosity (Nishita and Bean, 1979) while long chains of amylose restrict granule swelling thereby lowering peak viscosity of starch slurries (Patindol *et al.,* 2007; Jane *et al.,* 1999; Tester and Morrison, 1990). Thus high peak viscosity of Njavara and IR 64 can be attributed to its long chains of amylopectin. High content of hot water soluble polysaccharides lower the peak viscosity (Patindol and Wang, 2005). Thus the high solubility of Jyothi (Table 2) is responsible for its low peak viscosity. However, in the present study, the lipid and protein interactions with starch granules in the flour also play a role.

Hot paste viscosity is the viscosity measured at end of heating followed by cooking. In general, hot paste viscosity is always less compared to peak viscosity. The swelling of starch granules to the highest extent is shown by peak viscosity, after which these swollen granules bombard each other due to non availability of space for further swelling and hence breakdown of starch granules occurs leading to decrease in viscosity, indicated by the hot paste viscosity. Thus, hot paste viscosity is the degree of disintegration of gelatinized starch granules (Mazurs *et al.,* 1957). Among the values measured, Njavara registered highest hot paste viscosity (~670 BU) compared to other two non medicinal varieties implying easy disintegration of Njavara starch granules. The two non medicinal varieties registered almost same hot paste viscosity around 430-440 BU.

Cold paste viscosity is the viscosity measured at the end of cooling, stopped either at 50° C or 30° C (Halick and Kelly, 1959). It also indicates the stability of the cooked paste. Cold paste viscosity is generally higher than the peak viscosity due to association of broken granules, in other words it is the precipitation of linear molecules present in the system. This precipitation of linear molecules in turn increases the viscosity. The phenomenon is termed as retrogradation. Cold paste viscosity was observed to be high for Njavara compared to Jyothi and IR 64.

Breakdown is a derived parameter, difference between the peak viscosity and the hot paste viscosity. It reflects the stability of the paste during cooking. Break down values were 210 BU, 170 BU and 70 BU for IR 64, Njavara and Jyothi respectively. Least susceptibility of cooked rice to disintegration was seen for Jyothi and more for IR 64 variety. Njavara shows intermediate susceptibility of cooked rice to disintegration. Patindol et al. (2006) have reported positive correlation between peak and breakdown viscosity with percentage of short amylopectin chain. Accordingly, it can be concluded that Jyothi has the short amylopectin chains compared to Njavara and IR 64.

Setback is the difference between cold paste viscosity and peak viscosity. This indicates the precipitation of linear molecules while cooling or degree of hardening or retrogradation of cooked rice during cooling. It is associated with gel network formation that involves amylose and the long chains of amylopectin to hold the integrity of starch granules during heating and shearing (Patindol and Wang, 2003). Higher set back values are observed for Njavara whereas almost similar values are noticed for the non-medicinal rice, indicating higher retrogradation in Njavara rice. Total set back is the difference between cold paste viscosity and hot paste viscosity also called consistency (Merca and Juliano 1981; Perez and Juliano 1979). Total set back indicates total precipitation of linear molecules of starch or amylose molecules in general at the end of cooling. It is observed that medicinal rice shows highest value of ~1055 BU followed by IR 64 (826 BU) and Jyothi variety (710 BU).

Relative breakdown shows breakdown of starch granules in the sample compared to total set back. The relative breakdown is found to be high in IR 64 (0.25) compared to the pigmented varieties, Njavara (0.16) and Jyothi (0.10). Thus, in aqueous medium the viscography parameters for the Njavara rice are highest among the three rice varieties studied under the present programme of work.

The gelatinization temperature varied among the three rice varieties, highest in non-pigmented rice IR 64 and low in pigmented rice Njavara and Jyothi. In milk medium the swelling behaviour, loss of birefringence and gelatinization temperature differs because of the usual constituents of milk (Table 4) which has been adopted from literature (Briard *et al.,* 2003; Jensen, 2000).

Peak viscosity is found to be highest in IR 64 (885 BU) followed by Jyothi (635 BU) and least in medicinal rice (590 BU). This phenomenon is due to high swelling of starch granules of IR 64 and least swelling in medicinal rice, in milk medium. Hot paste viscosity also follows similar pattern, IR 64 registered highest value followed by Jyothi and Njavara, again indicating the fact that in milk medium the breaking of granules after complete swelling was highest for IR 64 and least for medicinal rice. Cold paste viscosity registered by IR 64 and Jyothi appeared almost similar and least in medicinal rice indicating the fact that on cooling the precipitation of the linear molecules in Njavara is less (~300 BU) compared to the two non medicinal rice studied. Breakdown is observed to be high in IR 64, around 200 BU while almost same in Jyothi and Njavara.

Table 4. Composition of Cows milk

Main Components	% Composition	Sub Components: Components	Sub Components: %Composition
Water	86.1		
Lactose	4.4 - 4.9		
Protein	3.1-3.8		
		Casein	80
		Whey proteins	20
Lipid	3.5 - 3.9		
		Fatty acids	
		Myristic acid (14:0)	13 -14.2
		Palmitic acid (16:0)	30.2 - 42.7
		Stearic acid (18:0)	5.7 -13.7
		Oleic acid (18:1)	16.7 - 27.1
		Linoleic acid (18:2)	1.6 -3.0
		Linolenic acid (18:3)	0.5 -1.8
		Triglycerides	97
		Phospholipids	1.5
		Unsaponifiable matter	1.5
Ash	0.7 - 0.8		

Setback values were observed to be high in milk medium. IR 64 and Jyothi showed high values and least by medicinal rice. Higher value of setback in IR 64 indicates that after reaching the peak viscosity, the precipitation of linear molecules are more while cooling the sol compared to other two varieties. Total set back is highest in Jyothi (1355 BU) in milk medium, followed by IR 64 (1810 BU) and Njavara (1045 BU). It is also an indication that retrogradation which begins immediately after end of cooking phase i.e. from 95°C to 95°C and 95°C to 30°C, the viscosity is highest in Jyothi, a non medicinal pigmented rice. However, in medicinal rice precipitation is less; hence the retrogradation is also less. Relative breakdown was also high for IR 64 in milk medium which is around 0.1 followed by Njavara (0.05) and Jyothi (0.03).

The gelatinization temperature, in aqueous and milk media, for the varieties, except IR 64, did not differ much, indicating the fact that loss of birefringence and crystalline order of the starch granules in Njavara and Jyothi appears at the same temperature in both the media while the starch granules in IR 64 swells at a higher temperature, in milk media. Rice starches having short average amylopectin branch chain lengths display low gelatinization temperatures (Zhou *et al.,* 2002). The low gelatinization value of Jyothi, compared to Njavara and IR 64, may be due to variation in size and/or short average amylopectin branch chain lengths in starch molecule.

Peak viscosity in Njavara showed a higher value in aqueous medium because while heating the slurry, the granules swell to a maximum extent by losing the birefringence. The fibrous nature of Njavara (Deepa *et al.,* 2008) compared to Jyothi and IR 64 may be responsible for higher absorption of moisture, leading to high peak viscosity in aqueous medium. In milk medium the swelling of starch granules is possibly hindered due to proteins, fat and other constituents in milk. However, in non-medicinal rice the constituents of the milk medium favour the swelling of starch granules. Paulsson and Dejmek (1990) have reported that at high temperatures milk whey proteins especially α-lactoalbumin and β-lactoglobulin denature leading to aggregation which in turn increases the viscosity. The denaturation of milk proteins could be one of the factors responsible for higher peak viscosity of rice flour in milk medium than aqueous medium. Noisuwan *et al.* (2008) reported that the addition of different milk proteins affect the pasting behavior in normal rice variety because of high amylose content. Lower peak viscosity of Njavara in milk medium compared to aqueous medium, though the amylose content is similar to that of non-medicinal varieties, indicate unique property of Njavara starch and warrants an in-depth study to understand its usage in ayurvedic preparations. Even the non-starchy polysaccharides present in Njavara may be playing a role in reducing the parameters in milk medium.

In non-medicinal rice varieties milk favors less starch granule breakdown and hence the hot paste viscosity values are high, to an extent of 200 to 250 BU. Interestingly, the cold paste viscosity is less in medicinal rice in milk medium, indicating the possibility that the precipitation of linear molecules in Njavara is comparatively less compared to aqueous medium while high in Jyothi and in IR 64.

Among the derived parameters breakdown is highest in aqueous medium. Breakdown value indicates susceptibility of cooked rice (gelatinized starch granules) to disintegration (Juliano *et al.,* 1985). However, in milk medium the swelling of starch granules are relatively less hence the viscosity, peak viscosity and breakdown value are relatively low compared to aqueous medium. Peak viscosity values also show that in milk medium the swelling is more in non medicinal rice varieties and less in medicinal rice.

Setback values are less in aqueous medium indicating the fact that precipitation of linear molecules are less, however the phenomena is quite opposite in milk medium, where these values are high, the extent of precipitation of linear molecules occurs in the following increasing order IR 64 >Jyothi > Njavara. These values indicate that occurrence of retrogradation is quite high in milk medium which needs in depth studies in future. Total setback was almost same in aqueous

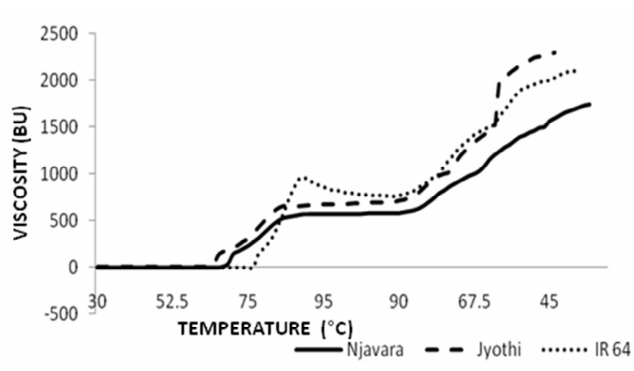

Fig. 2. Viscograms of dehusked rice of Njavara, Jyothi and brown rice of IR 64 in milk media

and milk media in the case of medicinal rice i.e. complete precipitation occurs to almost same extent. In non-medicinal rice milk medium facilitates the linear molecules to accumulate from linear as well as lengthy linear portion of branched molecules of starch granules such that precipitation occurs to a higher extent and hence high set back values.

Relative break down values are high in aqueous medium. In milk medium the values decreases almost to one third.

In Ayurveda, the temperature of Njavara *kizhi* is maintained above 80 ºC throughout the treatment, by reheating in a decoction of milk and herbs. Thus, assuming heat content of the bolus plays a crucial role in the treatment DSC studies was carried out in Njavara along with non medicinal rice varieties. DSC is a thermodynamic approach which helps to monitor the physical and chemical changes occurring in the starch molecules during gelatinization (Donovan *et al.,* 1983). Details of enthalpies and transition temperatures associated with gelatinization of dehusked rice flour of Njavara, Jyothi and brown rice of IR 64 are summarized in Table 3 and the thermograms of the flour samples are shown in Figure 3. Thermal curves generated by the calorimeter indicating rice starch gelatinization are characterized by three temperatures - Onset (To), peak (Tp) and conclusion (Tc) and by gelatinization enthalpy (ΔH), expressed as J/g. Generally To values indicate the start of gelatinization temperature. Among the native brown rice flour, in both water and milk media, IR 64 showed the highest gelatinization temperature of 69.4ºC

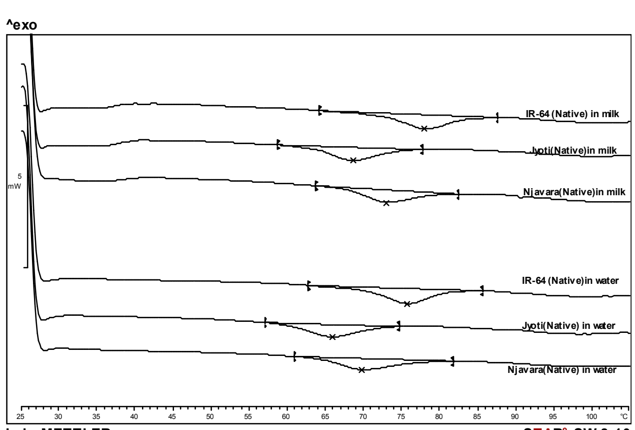

Fig. 3. DSC thermograms of native brown rice of Njavara, Jyothi and IR 64 in aqueous and milk media

and 72.1ºC followed by Njavara of 63.8ºC and 67.5ºC and Jyothi of 59.6 ºC and 62.9ºC, respectively. Gelatinization temperatures depend on sample concentration and flour type (Saif *et al.,* 2003).In the present study, the sample concentrations are kept constant (1:3, sample : media), thus the differences observed in thermograms are due to differences in rice variety. The difference in onset temperature can be attributed to various factors like amylose-amylopectin ratio, granular size and architecture (crystalline/ amorphous), molecular structure of amylopectin (chain length and branching) and presence of phosphate bond (Gunaratne and Hoover, 2002). Jyothi had low To, Tp and Tc values compared to Njavara and IR 64, which may reflect the presence of abundant short chains of amylopectin (Noda *et al.*, 1998). IR 64 had high transition values and Tp of 75.4 ºC and 78 ºC, in aqueous and milk media, respectively. This may be due to the presence of long chains of amylopectin molecules associated with the starch granules that require more energy for melting, as depicted by the high enthalpy values compared to Njavara and Jyothi (Table 3) (Yamin, *et al.,* 1999). The To, Tp and Tc values of IR 64 brown rice flour are comparable to those reported in case of IR 64 starch by Singh *et al.* (2007). The high gelatinization value of Njavara compared to Jyothi may be attributed to the smaller granular size and compact nature of starch granules in Njavara (Deepa, *et al.,* 2008).The gelatinization range (R) was observed to be more for Njavara (13.45) followed by Jyothi (12.62) and IR 64 (11.29) in aqueous media while in milk media there was no significant difference (~12). The difference in gelatinization range is attributed to the heterogeneity of crystallites of amylopectin molecules within the starch granules (Hagenimana, *et al.,* 2005). In general, cooking in milk medium increased the onset (To) and peak (Tp) temperature of all the three varieties.

The gelatinization temperature (To) and peak temperature (Tp) determined by DSC are observed to be lower than that measured by Brabender viscoamylo-graphy. Similar results have been reported by Noisuwan et al. (2008) and Qian and Kuhn (1999). Differences in the parameters determined by DSC and Brabender viscoamylo-graphy could be due to shear forces which play an important role in Brabender viscoamylo-graphy while sedimentation (i.e. phase transition) in DSC. Secondly, in DSC gelatinization occurs in a closed system (sealed cups) thus increasing the vapour pressure and facilitating the starch granules to absorb more moisture resulting in lower gelatinization temperature, compared to those determined by Brabender amylography. Thirdly, the peak temperature (Tp) measured by DSC represents the temperature at gelatinization of starch granules is maximum while peak viscosity, measured by Brabender, corresponds to the point of maximum starch granule volume (Noisuwan, et al., 2008). The study showed that IR 64 has longer chains of amylopectin, requiring higher temperature to dissociate completely than required for shorter chains, as in Jyothi.

X-ray diffraction pattern of native rice flour is illustrated in Figure 4. The X-ray diffraction pattern was comparable to those reported earlier for rice starches (Singh *et al.,* 2007; Ratnayake and Jackson, 2007). The main crystalline peaks in the X-ray diffraction pattern are attributed to the crystalline peaks

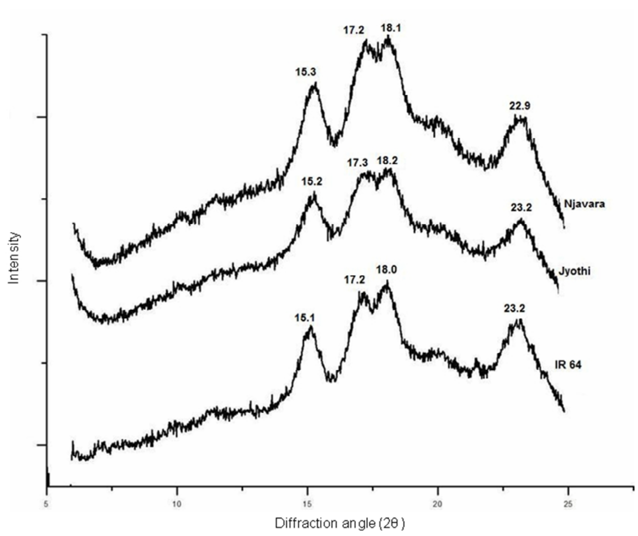

Fig. 4. X-ray diffractogram of native brown rice of Njavara, Jyothi and IR 64.

of starch. The granule crystallinity is ascribed to amylopectin components in starch. Four stronger diffraction peaks were observed around 2θ values of 15° (d spacing 5.8 Å), 17° (5.2 Å), 18° (4.9 Å) and 23° (3.8 Å). This peak pattern is associated with 'A' form of starches common in all cereal starches (Zobel, 1988). The effect of moisture content on the % relative crystallinity was neglected since the moisture contents of all samples were almost the same (~13%). Jyothi flour showed weak A-type pattern with lower peak intensities compared to Njavara and IR 64 indicating the lower crystallinity. According to Singh *et al.* (2006 a, b) higher amount of long chains of amylopectin increases crystallinity.The percentage of relative crystallinity of Njavara, Jyothi and IR 64 was observed to be 21, 20 and 26 respectively. The difference in crystallinity structure may be attributed to fine structures of each starch component i.e. proportion of amylose, short and long chains of amylopectin (Noda *et al.*, 1998). The lesser cystallinity of Jyothi may be due to relative amounts of very short amylopectin chains which lower molecular and crystalline order and a non-optimized packing within the crystalline lamellae (Vandeputte *et al.,* 2003a) thereby decreasing the gelatinization temperature. While longer amylopectin chains form longer double helices within the crystalline lamellae of starch granules thus increases crystallinity and delaying gelatinization as seen in case of IR 64.The d-spacing 4.4Å is characteristic of amylose-lipid/protein complex (Liang and King, 2003). The peak intensity at 4.4Å was observed to be of the order Njavara>Jyothi>IR 64.

The medicinal rice Njavara behaved quite differently with respect to viscographic properties compared to non medicinal rice in aqueous and milk media. In milk medium, the medicinal rice showed relatively lesser values when compared to aqueous media. The variation in interaction of milk components like protein, sugars and lipids with Njavara rice starch and non-medicinal rice starch could be responsible for the differences in the pasting behavior and needs further investigation to elucidate the use of Njavara cooked rice in ayurvedic preparation of Njavara *kizhi*. The swelling and precipitation of linear molecules appears to be very less in milk medium in Njavara, hence the bolus will be less bulky in size and also weight. This less bulky semi hot bolus of Njavara makes it convenient for the ayurvedic doctors to massage the body of patient by dipping it in medicinal herb decoction. The interaction of milk, Njavara starch with medicinal herb extract needs to further be investigated to understand the role of Njavara rice in ayurvedic treatment.

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