African Journal of Food Science. Vol (2) pp. 102-111, September, 2008
Available online http://www.academicjournals.org/ajfs
ISSN 1996-0794 ©2008 Academic Journal

Full Length Research Paper

Some properties of starches from cocoyam (*Colocasia esculenta*) and cassava (*Manihot esculenta* Crantz.) grown in Malawi

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Accepted 15 September, 2008

The physicochemical and functional properties of starch from cocoyam and ten varieties of cassava grown in Malawi were studied to unravel their potential in industrial application. The properties of starch varied significantly with crop and among varieties. Cocoyam starch granules exhibited polygonal truncated shapes and small sizes (average of 7 µm) while the cassava starch granules were rounded, irregular with oval and truncated ellipsoidal-granules with average size of 10.14 µm. The cocoyam starch gave lower values of amylose values content and paste clarity but higher phosphorus content, maximum wavelength of iodine complex absorption and blue value than cassava starches. Cassava starches gels were more stable to freeze thawing releasing 28.40 – 46.92% of the water than cocoyam which released 54.06% of its water. Swelling and solubility of both cocoyam and cassava starches increased with temperature (60 - 90°C). Cocoyam starch exhibited lowered swelling power and solubility than cassava starches. The studies of gelatinization and retrogradation characteristics indicated similar enthalpy values of gelatinization of cocoyam and cassava starch; cocoyam starch displayed higher retrogradation tendencies than cassava starches.

Key words: Cocoyam, cassava, amylose, blue value, swelling, solubility, paste, freeze-thaw, gelatinization, retrogradation.

INTRODUCTION

Starch is a major component of plant foods and an important raw material for industry. In Malawi starch is widely used to manufacture various products such as food, textiles, pharmaceuticals, dry cells and adhesives. Utilization of native starch in industries is limited by its functional and physicochemical properties. Botanical source, environmental conditions and varietal differences are known to influence the functionality of starches (Peroni et al., 2006; Srichuwong et al., 2005; Riley et al., 2006; Tester et al., 2004).

Starches used in Malawian industries largely constitute those of maize, potato and wheat, which are imported from Zimbabwe, South Africa, the Netherlands, United Kingdom and Tanzania. Importation of starch leads to loss of large amounts of foreign currency, and increased unemployment (NSO, 1999; Masumbu, 2002). Therefore, there is need for an indigenous crop locally grown by subsistence farmers that will help bring direct economic benefits to those who need it most. Starch has two major components: amylose and amylopectin. These polymers are very different structurally. Amylose is a relatively long, linear polymer α-glucan containing around 99% (1→4)-α- and 1% (1→6) linkages while amylopectin is a much larger molecule and a heavily branched structure built from about 95% (1→4)-α- and 5% (1→6)-α- linkages. The structures of these polymers play a critical role in the functionality of native and modified starches. Viscosity, shear resistance, gelatinization, solubility, gel stability and retrogradation are some of the functional properties that depend on the amylose/amylopectin ratio of the

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the starches (Tziotisa et al., 2005; Chakraborty et al., 2004).

Cassava (*Manihot esculenta* Crantz.) and cocoyam (*Colocasia esculenta*) are potentially important sources of starch in Malawi. Unlike cassava, cocoyam starch has not been exploited in local industries. Lack of information on the properties of starches from cassava and cocoyam produced in Malawi has contributed to limited utilization of these starches in industry. Knowledge on properties of the starches from these crops therefore would unravel the opportunities offered by these root crops and help their utilization. This paper, therefore, concerns some characteristic properties of the starches from cassava cultivars and cocoyam grown in Malawi that will help in industrial utilization of the starches.

MATERIALS AND METHODS

MATERIALS

The study used starch isolated from ten cassava varieties. Cassava varieties included were the local recommended varieties: Mbundumali, Maunjili, Silira and Mkondezi, locally screened varieties: Sauti and CH92/082, and introduced varieties from IITA: 83350, TMS4(2)1425, 81/00015 and LCN 8010 (Benesi, 2005). Cocoyams were purchased from Masasa, Mzuzu, Malawi and starch was extracted as follows: fresh tuberous roots were washed, peeled, washed again, chopped to about 1 cm^3 cubes and transferred into a heavy duty blender (Waring Commercial, model CBCSA 33BL34). One litre of water was added to 500 g of the chopped tubers, and the chopped tubers were pulverized at a high speed for 5 min. The suspension was then filtered using a double cheese (muslin) cloth. The filtrate was allowed to stand for four hours to facilitate starch sedimentation and the top liquid was decanted and discarded. The sediment was resuspended in 1 L of water and the whole process was repeated three times. The sediment was then washed and dried in the sun (open air) for two days.

METHODS

Moisture content

Moisture content was determined in duplicate by drying starch samples of 2 - 3 g in an air oven at 105°C overnight. The samples were cooled in a desiccator for 1 h and weighed to 1 mg to determine weight loss. Moisture content (MC) was calculated in percent (%) of sample.

pH

Starch samples (5 g) were weighed in duplicate in a beaker, mixed with 20 mL of distilled water, the resulting suspension stirred for 5 min and left to settle for 10 min. The pH of the water phase was measured using a calibrated pH meter (Benesi, 2005).

Ash content

Duplicate sets of crucibles containing dried starch samples (2 - 3 g) were placed in a muffle furnace at 525°C for 5 h, then cooled in a desiccator and weighed. Ash content was determined by weight difference and expressed as a percentage.

Phosphorus content

Phosphorus was determined by a modified method of Riley et al. (2006). Starch samples (2 g) were weighed into 150 mL ceramic beaker, ashed at 550°C for 5 h, cooled in a desiccator, mixed with 100 mL of 1 M HCl followed by addition of 1 mL of 1M HNO_3. The resulting mixture was heated to boiling, cooled, transferred to a 100 mL volumetric flask and made up to volume with water. Aliquots (1 mL) in triplicates were transferred to test tubes mixed with 9 mL of Murphy-Riley solution (Murphy and Riley, 1958), left to stand for 15 min and absorbance at 880 nm read against a reagent blank.

Granule morphology

Granule morphology of the native starches was studied using scanning electron microscopy (SEM). Starch samples were mounted on circular aluminium stubs using adhesive and then coated with thin layer of gold using Bio-Rad sputter coating system. The samples were examined and photographed in a Jeol Scanning Microscope (JSM-6400, Tokyo, Japan) at an accelerating voltage of 5 kv and a magnification of x1000, x2000 and x3000. Twenty granules were selected randomly and their size measured using a ruler.

Water holding capacity

Water holding capacity (WHC) was determined by centrifugal procedure. Starch samples (1 g) were suspended in 15 mL of distilled water in pre-weighed centrifuge tubes, slurry shaken on a rocking shaker for 1 hour and centrifuged at 12,100 x g for 10 min. The free water removed carefully from the wet starch and the weight of wet starch was determined. WHC was calculated as the ratio of mass of water absorbed to mass of dry starch.

Swelling power and solubility patterns

Swelling power was determined by dispersing 0.5 g of starch samples in 20 mL of distilled water in a pre-weighed centrifuge tubes. The slurries were heated in a thermostatically controlled water bath at 60, 70, 80 and 90oC for 30 min with shaking every 5 min to keep the starch granules suspended. The heated slurries were then cooled to room temperature and centrifuged at 12,100 x g for 10 min to separate gel and supernatant. The supernatant was decanted carefully and poured into dish for subsequent analysis of solubility pattern. Weight of swollen starch was determined and swelling power was determined as the ratio of the weight of the swollen starch to the weight of the starch sample.
To determine solubility of the starches, supernatant was transferred into a pre-weighed evaporating dish and dried in air oven at 105□C for 4 h. Weight of the residue was determined and the water solubility index was calculated from the amount of dried solids recovered by evaporating the supernatant and expressed as gram dried solids per 100 gram of sample on dry weight basis (Chiang et al., 2007).

Paste clarity and stability

The paste clarity was determined according to the method of Craig et al., (1989). A 1% aqueous suspension was made by suspending 0.2 g (db) starch in 20 mL of distilled water in a stoppered centrifuge tube and vortex mixed. The suspension was heated in a boiling water bath for 30 min thoroughly shaking every 5 min. After cooling, clarity of starches was determined by measuring percent transmittance at 650 nm against a water blank on a spectrophotometer (Spectronic Unicam, Heλios, Cambridge, United Kingdom). Samples used to determine paste clarity were stored at 4°C (in a refrigerator) for six days and the percentage transmittance was measured after every 24 h for the period of storage.

Freeze-thaw stability (syneresis)

Net syneresis of gels from starch pastes was determined according to the method of (Schmitz et al., 2006). Starch paste was prepared by heating a 5% starch suspension (1.0 g starch in 20 mL of distilled water) at 95°C for 30 min with constant shaking (every 5 min). Starch paste was weighed into polypropylene centrifuge tubes and submitted to successive cycles of freezing and thawing. The gels were stored at -18°C for 18 h (two tubes per sample) and thawed to 30°C for 90 min in a water bath. The thawed gels were vortexed for 15 s then centrifuged at 24,200 x g for 10 min. The amount of water eliminated from the gel was weighed. Four freezing and thawing cycles were performed and syneresis was calculated as a percentage of the total weight of gelatinized samples.

Amylose contents

Amylose content was determined using an Amylose/Amylopectin Assay Kit (Megazyme International Ireland Ltd., Bray, Ireland). In this method starch samples are completely dispersed by heating in dimethyl sulphoxide, and lipids are removed by precipitating the starch in ethanol. Precipitated starch is recovered by centrifugation and dissolved in acetate buffer solution. Amylopectin is specifically precipitated by addition of concavanalin (Con A) and removed by centrifugation. Amylose in the aliquot is determined using glucose/peroxidise reagent (GOPOD) after enzymatic hydrolysis to glucose. Total starch in separate aliquot is determined using GOPOD reagent after hydrolysis to glucose and concentration of amylose is estimated as the ratio of GOPOD absorbance at 510 nm of the supernatant of Con A precipitated sample, to that of total starch sample (Gibson et al., 1997).

Iodine absorption spectra and blue value

Iodine spectra of the native starches were determined by DMSO-urea method of Van Hung and Morita (2005). Starch (40 mg) was dispersed in 10 mL of 10%-urea containing dimethyl sulphoxide (90% DMSO, 10% 6M urea) by vigorous vortexing, heated in a boiling water bath for 20 min and cooled to room temperature. Aliquots (0.5 mL) of the dispersion were transferred in triplicates to a 25 mL volumetric flask, mixed with about 20 mL of distilled water and 1 mL of iodine-potassium iodide (200 mg I_2 and 2 g KI in 100 mL distilled water) solution,and filled to the mark. The mixture was stood for 20 min at room temperture and an absorption curve was measured from 500 to 800 nm with a spectrophotometer (Spectronic Unicam, Heλios, Cambridge, United Kingdom). Blue value (BV) of the starches was determined as absorbance measured at 680 nm.

Differential scanning calorimetry

Thermal analyses of starch samples were obtained using differential scanning calorimetry (DSC 822e, Mettler, Toledo, Switzerland) using starch: water ratio of 1:1. Starch samples of 3.0 mg were weighed into DSC aluminium pans. Distilled water, 3 µL, was added to starch sample using a transfer pipette and the pans were then sealed, and the samples were left to stand for 2 h at room temperature for moisture equilibration. The sealed pans were then heated from 25 to 120°C at a heating rate of 10°C/min to gelatinize the starch samples. From the DSC thermograms onset temperature (T_o), peak temperature (T_p), conclusion temperature (Tc) and enthalpy of gelatinization (ΔH_G) were determined using instruments software (Star SW 9.00). Temperature range and peak height index (PHI) were also calculated as $T_c - T_o$ and as the ratio $\Delta H_G/(T_p-T_o)$ respectively. Retrogradation of the starch was also determined using differential scanning calorimetry. The gelatinized samples were stored at 4°C (refrigerator) for periods of 1 and 7 days. After each period the samples were equilibrated at room temperature for 2 h, and then rescanned in the calorimeter from 20 to 120°C at 10°C/min to measure the retrogradation transition temperatures and enthalpy. The degree of retrogradation was determined as the ratio of enthalpy change of retrograded starch to enthalpy change of gelatinized starch (Gunaratne and Hoover, 2002).

Statistical analysis

Data obtained was subjected to analysis of variance (ANOVA) at the significant level of 5% ($\alpha \leq 0.05$) using Statistix 8 for windows software (Analytical software, Tallahassee, USA). When statistical differences were found, the least significant difference (LSD) was used to compare means at the 5% significance level. Correlations between physicochemical properties were also evaluated.

RESULTS AND DISCUSSION

Composition of the starches

Results of analysis of moisture, ash, amylose and phosphorus contents the starches are presented in Table 1.

Moisture content of the starches ranged from 10.42 to 11.13%. Ash contents of the starches ranged from 0.10 to 0.20%. Cocoyam starch had ash content (0.14%) similar to the cassava starches. pH of cocoyam starch (6.3) was higher than that of cassava starches (5.1 - 6.0). Amylose content of the starches ranged from 16.27 to 28.82% and varied significantly ($p < 0.001$) with its source. Cocoyam starch had lower amylose content than cassava starch. Amylose content ranged from 16.96 to 28.83% for cassava varieties, with Silira having the lowest and 81/0015 the highest. Phosphorus in starch exists mainly in two forms: phosphate-monoesters and phospholipids. Root and tuber starches contain phosphorus in the form of mono phosphate esters covalently bonded to starch while phospholipids are predominant in cereal starches. Phosphorus contents of starches vary with botanical source, maturity as well as growing environment (Jane et al., 1996). Phosphorus content of the starches ranged from 65.35 to 128.72 mg/kg (0.0063 to 0.013%) and varied significantly ($p < 0.001$) with source. Cocoyam starch had higher phosphorus content (119.15 mg P/kg, 0.012%) than most of the cassava varieties. Mkondezi, Silira and CH92/082 cassava varieties had the lowest phosphorus contents while TMS4(2)1425 had highest. Value ranges of 13.6 to 23.8% and 3 - 43% for amylose content, and, 0.007 - 0.012% and 0.006 – 0. 013% for phosphorus contents have been reported for cassava and cocoyam respectively (Moorthy, 2002). Our results are therefore similar to those reported except for 83350, CH92/082, 81/0015 cassava varieties which had amylose content and TMS4(2)1425 had higher phosphorus content.

Table 1. Granule size distribution, moisture content (MC), ash content (AC), pH, amylose content (AM), phosphorus content (P), water binding capacity (WBC), paste clarity (PC), maximum wavelength ($\lambda_{max,}$) and blue value (BV) cocoyam and cassava variety starches.

Starch source	Granule size distribution			MC %)	Ash (%)	pH	AM (%)	P (mg/kg)	WBC (g /g)	PC (%T)	λ_{max} (nm)	BV
	size range (µm)	Mode (µm)	Average size (µm)									
cocoyam	2.78 – 13.88	3.33	7.00	10.42	0.14	6.3	16.27^{g}	119.15^{a}	0.90	22.83^{e}	614.5^{a}	0.329^{a}
81/00015	4.44 – 17.78	10.00	10.66	10.85	0.14	5.6	28.25^{a}	95.32^{b}	0.93	44.16^{ab}	583.5^{c}	0.234^{d}
83350	4.44 – 15.56	11.67	10.52	10.57	0.13	5.1	24.27^{c}	73.34^{cd}	0.93	48.64^{a}	602.7^{b}	0.272^{bc}
CH92/082	4.44 – 15.00	6.11	9.38	10.75	0.15	5.5	26.56^{b}	65.34^{d}	0.98	41.24^{bc}	596.5^{b}	0.248^{cd}
LCN8010	5.56 – 17.22	10.00	10.56	10.74	0.16	5.7	21.20^{e}	72.88^{cd}	1.08	49.51^{a}	598.0^{b}	0.276^{b}
Maunjili	4.17 – 13.89	7.78	9.61	10.73	0.10	5.1	19.20^{f}	76.59^{bcd}	0.99	27.74^{e}	597.5^{b}	0.270^{bc}
Mbundumali	5.00 – 16.67	12.22	12.07	10.76	0.19	5.7	19.48^{f}	79.56^{bcd}	1.00	35.76^{cd}	596.7^{b}	0.279^{b}
Mkondezi	2.78 – 22.22	13.33	11.01	10.63	0.14	5.7	19.73^{f}	70.18^{cd}	0.94	43.96^{ab}	596.8^{b}	0.289^{b}
Sauti	2.78 – 15.56	5.56	8.38	10.87	0.10	5.1	22.68^{d}	87.58^{bc}	0.97	40.66^{bc}	598.8^{b}	0.247^{cd}
Silira	3.32 – 12.50	10.56	8.15	11.13	0.16	5.5	16.96^{g}	68.18^{cd}	1.01	33.81^{d}	597.0^{b}	0.264^{bc}
TMS4(2)1425	5.56 – 14.44	14.44	9.82	10.88	0.12	5.3	18.61^{g}	128.72^{a}	0.86	34.67^{d}	598.3^{b}	0.277^{b}

NB: Means followed by the same letter within the same column are not significantly different from each other (P = 0.05).

Microscopy of starch granule shapes and size

The size and distribution of starch granules is important for specific applications (Wang, 1983) and this depends on botanical source and may vary among varieties of crop (Moorthy, 2002; Moorthy et al., 1993). Results of morphological appearance and size of cocoyam and cassava starches as determined by SEM are presented in Figure 1 and Table 1.

Cocoyam starch showed small and medium polyhedral (polygonal) and truncated granules (Figure 1a) and exhibited smooth surfaces with some portions of the surface being irregular. Granule size ranged from 2.78 to 13.88 µm with a mode of 3.33 µm and average of 7.00 µm. Shapes mostly spherical, 5- to 6-sided polygonal, small rounded, medium ellipsoidal-truncated and large polyhedral with size ranges of 0.05 - 0.08 µm, 2.96 – 5.19 µm and 0.5 to 5.0 µm have been reported (Maeda et al., 2004; Sefa-Dedeh and Kofi-Agyir Sackey, 2002; Moorthy et al.,1993; Pérez et al., 2005). The range of size of the granule in this study was comparatively large. Cassava starches showed small to large rounded, irregular with oval and truncated ellipsoidal-granules within the same sample (Figure 1 b-k). Just like cocoyam the starch granules had smooth surfaces with some portions being irregular. Granule size distribution varied substantially among the cassava varieties. Granule size ranged from 2.22 to 22.22 µm with an overall average of 10.14 µm. Mbundumali, and Mkondezi had the largest granule size while Silira and Sauti had the smallest. Using light microscopy, Benesi (2005) reported mostly round or oval shapes, with a flat surface on one side containing a conical pit which extended to a well for cassava starches. Granule sizes ranged from 4.3 to 24.3 µm. Other researchers have reported round, oval, truncated, cylindrical and spherical shapes for cassava starch granules with size ranges from 4 to 25.0 µm (Gunaratne and Hoover, 2002; Sriroth et al.,1999; Mishra and Rai, 2006). Our results are in agreement with these findings.

WBC, maximum wavelength (λ_{max}) and BV

WHC of the starches ranged from 0.86 to 1.08 g H_2O/ g starch (Table 1) and no significant variations with starch source were observed. Starch source had a highly significant ($p < 0.001$) influence on both the λ_{max} and blue value of the starches. Cocoyam starch had higher values of λ_{max} and BV than cassava starch (Table 1). The value of λ_{max} for the starch-iodine complex is related to the chain length of the starch molecules. As the chain length increases, so does the value of λ_{max} (Tetchi et al., 2007). The results

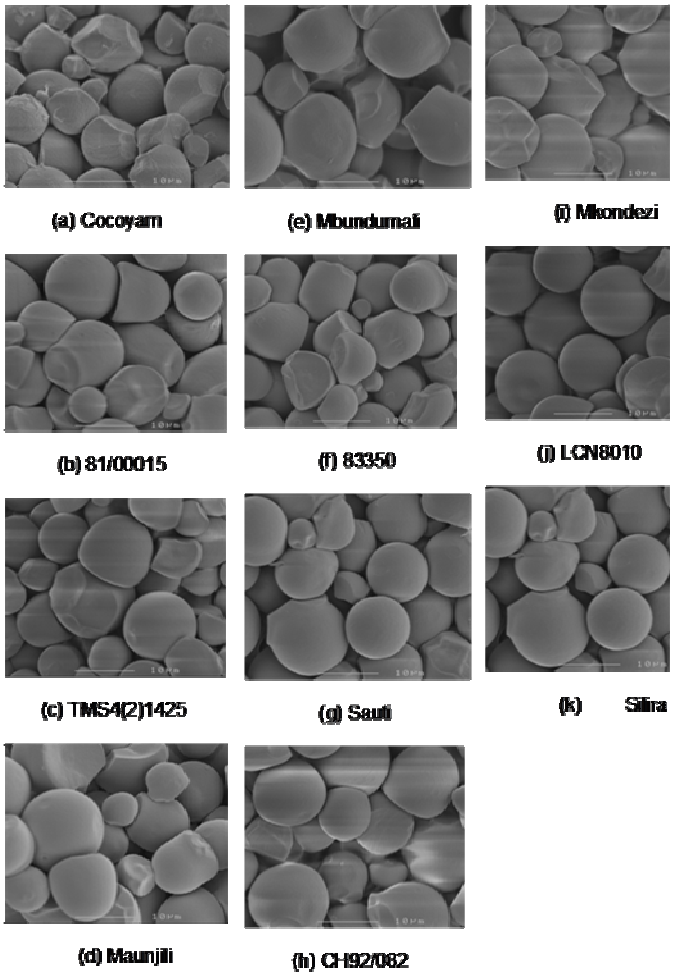

Figure 1. Scanning electron micrographs of the starch samples

therefore indicate the presence of longer chain starch molecules in cocoyam starch compared to cassava starches.

Freeze-thaw stability

Freeze-thaw stability, measured by degree of syneresis, describes release of water by gels that have been kept for longer periods refrigerated or frozen. This is an important factor to be considered when formulating refrigerated and frozen foods (Thomas and Atwell, 1999). Results of four cycles of freeze-thawing are shown in Figure 2. The amount of water released by the frozen starches differed significantly ($p < 0.001$). In the first cycle cocoyam starch, presented the highest tendency for water lost compared to the cassava starches draining 54.0% of the water, however in the second, third and fourth cycles, the amount of water released was within the range of cassava varieties. Among the cassava starches, LCN8010, Mbundumali, 83350 and Silira showed greater tendency to lose water draining 46.3, 45.3, 45.0 and 43.8% of the water while 81/00015 presented the least (28.4%). The percentage of water separated in the second, third and fourth cycles were low for all the starches indicating high stability at those cycles. LCN 8010 and 81/00015 cassava starches consistently showed high tendency to release water in the second, third and fourth cycle. Considering total amount of water released in all four cycles, gels from cassava starches exhibited lowest tendency to syneresis compared to cocoyam except LCN8010 starches. These results indicate that cassava starch is more stable to freeze-thawing than cocoyam starch and hence could be better suited for use in freeze products than coco yam starches. Among cassava starches, CH92/082, Sauti and Maunjili would be more suitable as they presented the highest freeze-thawing stability.

Paste clarity and stability

Starch gel clarity is a much desirable functionality of starches for its utilization in food industries since it directly influences brightness and opacity in foods that contain it as thickeners. Paste clarity and significantly ($P < 0.001$) varied with source (Table 1). Cocoyam starch paste exhibited lower clarity than the cassava starch pastes. Within the cassava cultivars, paste from LCN 8010, 83350, 81/0015 and Mkondezi starches had the highest clarity while Maunjili starch had the lowest. Amylose content is known to influence the clarity of starch pastes as lower amylose starches are easily dispersed, increasing transmittance and clarity. However our results are contrary to this observation. Cocoyam starch which showed the lowest clarity had comparatively lower amylose content (Table1). On the other hand, 83350 and 81/00015 starches which showed the highest paste clarity had higher amylose content except for Maunjili which had both lower paste clarity and amylose content. Correlation analysis showed a significant positive correlation of paste clarity with amylose content and granule (Table 4). These results suggest that paste clarity was influenced by so many factors, not only amylose to amylopectin ratio (Craig et al., 1989).

Usually processed foods are subjected to storage by refrigeration and during storage, retrogradation process occurs. Thus unaltered transparency during storage is a much desirable characteristic of starches used in food products (Schmitz et al., 2006). This functionality depends on the retrogradation characteristics of the starch. Retrogradation is a process where molecules comprising gelatinized starch reassociate into an ordered structure to retrieve a crystalline order, and during this process, the starch paste becomes increasingly more opaque (Thomas and Atwell, 1999). For the ten days of refrigerated storage applied, opacity of the cocoyam starch gel significantly increased compared with cassava starches indicating higher retrogradation tendency during storage (Figure 3).

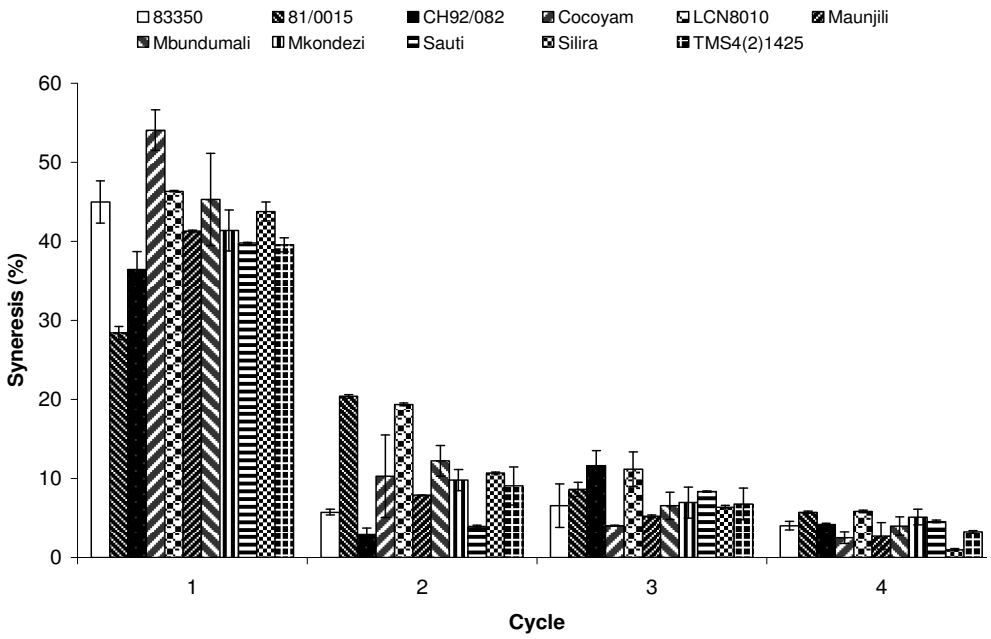

Figure 2. Syneresis (%) during freeze-thawing cycles of the starches.

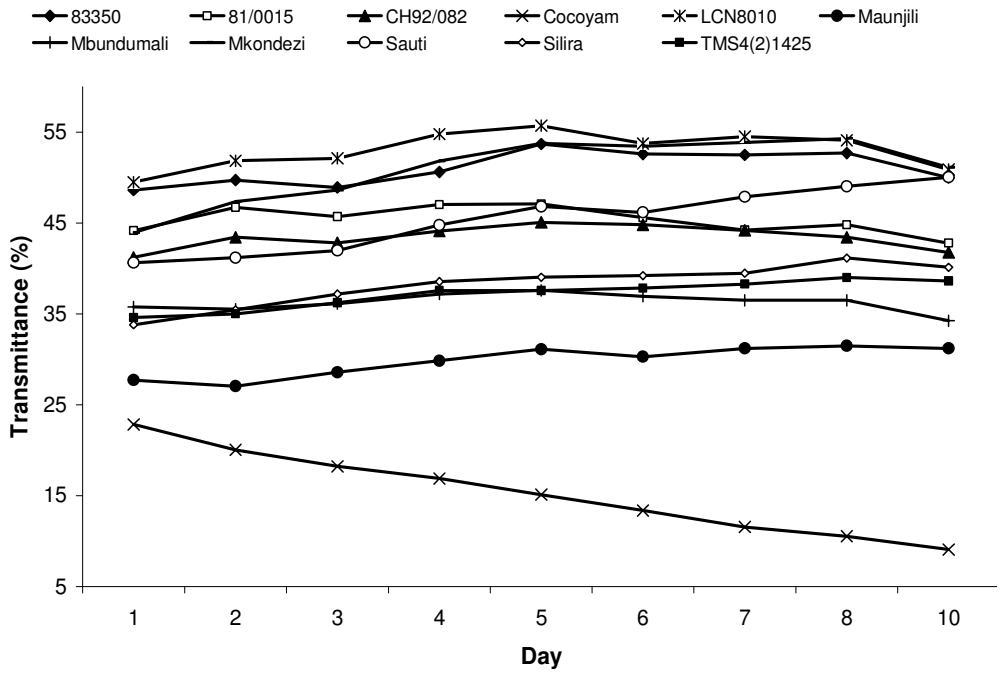

Figure 3. Effect of storage on gel light absorbance of some of the starches at 650nm.

Swelling power and solubility patterns

Solubility patterns of all starches at different temperatures are shown in Figure 4. Solubility increased as the temperature increased from 60 to 90°C. Generally cassava starches showed higher solubility at all temperatures compared to cocoyam starch. Silira and Sauti varieties showed significantly higher solubility than the other varieties at 70, 80 and 90°C however no cassava varieties showed consistently lower solubility at all temperatures. Swelling power of all starches showed similar pattern as the solubility (Figure 5) and source had significant effect

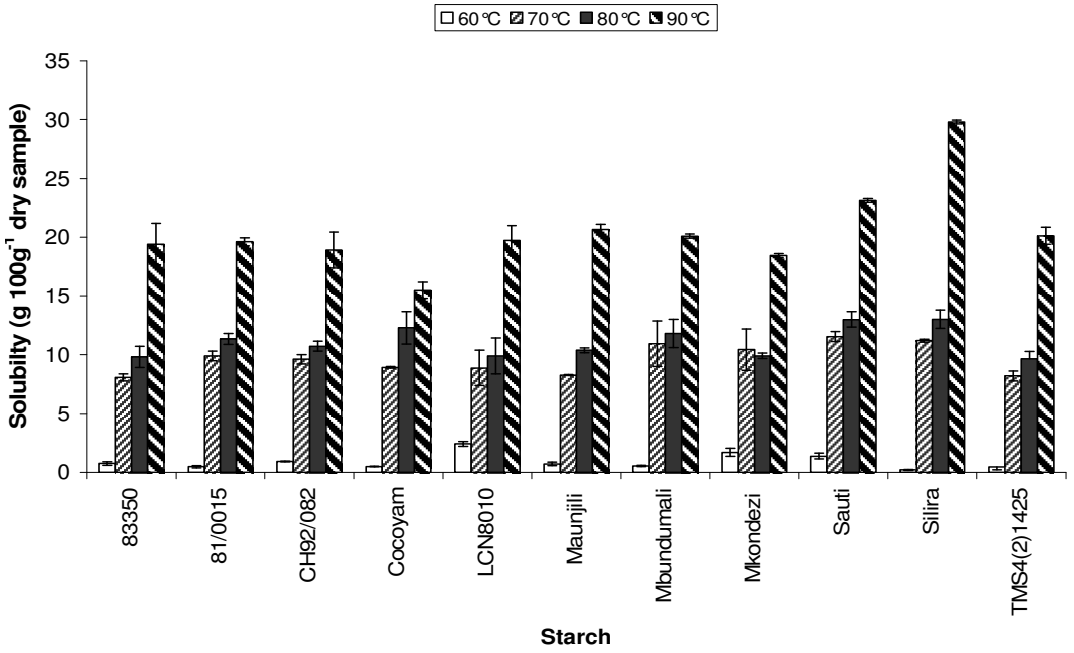

Figure 4. Solubility patterns of the starches

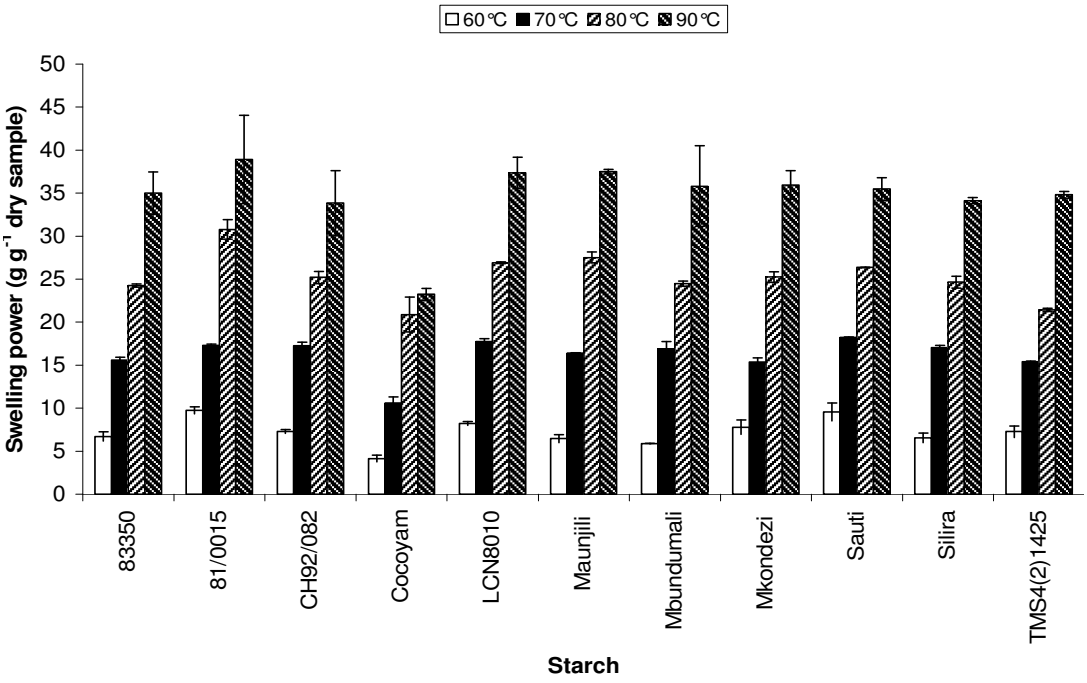

Figure 5. Swelling profiles of the starches.

on swelling power. Cocoyam starch exhibited lowest swelling power at all temperatures.

Maunjili, 81/00015, Sauti, LCN8010 and Sauti starches showed consistently higher swelling power than other cassava varieties while TMS4(2)1425 starch exhibited lowest swelling power. Thus botanical source variety had significant effect on swelling power and solubility of the starches under study.

The differences in solubility and swelling behavior indicate differences in the structure of starches. Differences in solubility could be attributed to different chain length distributions in the starches (Bello-Pérez et al., 2000).

Table 2. Thermal properties of the native starches

	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_G (J/g)	R (°C)	PHI
Cocoyam	59.88^{cde}	70.03^{a}	83.48^{ab}	11.43^{c}	20.31^{a}	1.12^{e}
81/0015	59.22^{de}	63.78^{d}	72.30^{d}	12.24^{bc}	9.12^{f}	2.68^{b}
83350	58.56^{eg}	66.74^{bc}	82.00^{abc}	12.74^{abc}	16.36^{b}	1.56^{de}
CH92/082	61.96^{ab}	66.96^{bc}	79.94^{abc}	11.41^{c}	9.99^{ef}	2.28^{bc}
LCN8010	57.63^{f}	63.77^{d}	76.32^{cd}	14.10^{ab}	12.28^{de}	2.30^{bc}
Maunjili	58.68^{ef}	62.84^{d}	85.08^{a}	13.73^{abc}	8.31^{f}	3.30^{a}
Mbundumali	62.48^{a}	67.41^{b}	79.70^{abc}	13.54^{abc}	9.86^{f}	2.76^{ab}
Mkondezi	60.80^{bc}	65.79^{c}	76.48^{cd}	13.63^{abc}	9.98^{ef}	2.74^{ab}
Sauti	59.46^{cde}	65.62^{c}	77.16^{bcd}	12.63^{bc}	12.32^{de}	2.05^{cd}
Silira	59.35^{de}	66.73^{bc}	80.08^{abc}	15.04^{a}	14.76^{bc}	2.04^{cd}
TMS4(2)1425	60.14^{cd}	66.68^{bc}	76.32^{cd}	11.77^{bc}	13.08^{cd}	1.80^{cd}

NB: Means followed by the same letter within the same row are not significantly different from each other (P = 0.05).

Table 3. Thermal properties of the retrograded starches

	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_G J/g)	R (°C)	PHI	% retrograd
Cocoyam	50.81^{a}	61.01^{a}	72.10	7.04^{a}	20.40	0.70^{a}	61.82^{a}
81/0015	48.71^{bcd}	57.44^{b}	65.10	4.44^{b}	17.48	0.51^{bc}	36.25^{bcd}
83350	48.67^{bcd}	58.24^{ab}	66.25	5.00^{b}	19.14	0.52^{bc}	39.25^{bcd}
CH92/082	50.01^{ab}	57.88^{ab}	64.40	4.63^{b}	15.75	0.60^{ab}	40.88^{bc}
LCN8010	48.74^{bcd}	58.26^{ab}	66.17	5.17^{b}	19.04	0.54^{bc}	36.67^{bcd}
Maunjili	48.01^{cd}	57.66^{ab}	67.24	4.86^{b}	19.29	0.50^{bc}	35.66^{bcd}
Mbundumali	47.54^{d}	56.66^{b}	63.85	4.24^{b}	18.22	0.46^{bcd}	31.28^{cd}
Mkondezi	47.71^{d}	57.10^{b}	64.73	4.08^{b}	18.78	0.44^{cd}	29.89^{d}
Sauti	49.60^{abc}	58.80^{ab}	64.05	4.10^{b}	18.28	0.45^{bcd}	32.46^{bcd}
Silira	47.86^{cd}	56.40^{b}	62.64	2.83^{c}	17.09	0.33^{d}	18.90^{e}
TMS4(2)1425	49.72^{abc}	58.60^{ab}	65.76	4.97^{b}	17.76	0.56^{abc}	42.40^{b}

NB: Means followed by the same letter within the same column are not significantly different from each other (P = 0.05)

Swelling power of starch depends on the capacity of starch molecules to hold water through hydrogen bonding. After gelatinization these hydrogen bonds between starch molecules are broken and are replaced by hydrogen bonds with water. Amylose content and proportion of outside-chains of amylopectin are thought to be major players in the water retention capacity of gel (Tang et al., 2005). Positive and negative significant correlations have been reported between swelling power with amylopectin unit-chain ratio and amylose content respectively (Srichuwong et al., 2005; Sasaki and Masuki, 1998). In this study swelling power had a positive significant correlation with amylose content (Table 4).

Gelatinization and retrogradation

Thickening and swelling are desired functionalities governing the use of starch in food industries as thickening agent in food products such as sauce. These two functionalities depend on gelatinization characteristics of starches (Karim et al., 2007). Starch gelatinization refers to the collapse of molecular order within the starch granule manifested in irreversible changes in properties as granular swelling, native crystalline melting, loss of birefringence and starch solubilization (Thomas and Atwell, 1999). Transition tem-peratures (T_o, T_p, and T_c) and ΔH_G for the gelatinized and retrograded starches are presented in Tables 2 and 3.

Thermal properties varied significantly ($p < 0.001$) among the starches. Cocoyam starch exhibited signifycantly higher T_p, and T_c values than the cassava starches however T_o was within the same range of cassava starches. Mbundumali exhibited high T_o, T_p, and T_c values among the cassava varieties while LCN8010 and 81/00015 consistently showed lower T_o, T_p and T_c values. ΔH_G was significantly lower for cocoyam starch compared to cassava starches but similar to that of CH92/082 variety. Silira and CH92/082 exhibited the highest and lowest ΔH_G respectively. PHI is the ratio of enthalpy of gelatinization to the temperature range and measures unifor-

Table 4. Correlations of the starch properties

	Amy	GS	Paste	T_o	T_p	T_c	ΔH_G	Range	PHI	ΔH_R	DR	Syn	SP	S
GS	0.2247													
Paste	0.552*	0.509*												
T_o	-0.029	0.312	-0.219											
T_p	-0.307	-0.298	-0.406*	0.570*										
T_c	0.401*	-0.178	-0.522*	0.284	0.415*									
ΔH_G	-0.467*	0.324	0.142	-0.022	-0.246	0.198								
Range	-0.327	-0.647**	-0.258	-0.308	0.606*	0.205	-0.254							
PHI	0.026	0.616**	0.117	0.255	-0.563*	0.030	0.560*	-0.899**						
ΔH_R	0.120	-0.203	-0.325	-0.049	0.333	0.258	-0.411*	0.431*	-0.375					
DR	0.056	-0.363	-0.364	-0.032	0.400*	0.142	-0.738**	0.494*	-0.568*	0.908**				
Syn	0.759**	-0.143	-0.328	0.034	0.470*	0.568*	0.360	0.512*	-0.215	0.420*	0.201			
SP	0.444*	0.229	0.455*	-0.452*	-0.818**	-0.483*	0.263	-0.499*	0.500*	-0.361	-0.430*	-0.507*		
S	-0.213	-0.087	0.109	-0.076	-0.160	-0.162	0.507*	-0.112	0.165	-0.735**	-0.733**	-0.081	0.104	
P	-0.029	-0.320	-0.438*	0.048	0.363	-0.065	-0.634**	0.374*	-0.510*	0.448*	0.618**	-0.121	-0.490*	0.018

*= $p<0.05$;**= $p<0.001$ Amy = amylose content; GS = Granule size; T_o = Onset temperature; T_p = peak Temperature; T_c = conclusion temperature; ΔH_G = enthalpy of gelatinization; Range = Temperature range; PHI = peak height index; ΔH_R = enthalpy of retrogradation; DR = Degree of retrogradation; Syn = Syneresis; SP = Swelling power (80°C); S = Solubility at 80°C; P = phosphorus

mity in gelatinization (Sandhu et al., 2005). Average PHI values ranged from 1.12 to 3.30. R values ranged from 8.31 to 20.31°C. Cocoyam had the highest R values compared to cassava starches. Among cassava cultivars Maunjili and 81/0015 cassava varieties had the lowest R values while 83350 had the highest.

The differences in gelatinization properties of starches are attributed to factors such as starch composition (amylose to amylopectin ratio, amount of lipid complexed, amylose chains, phosphorus content), molecular structure of amylopectin (unit chain and extent of branching), and granular architecture (crystalline to amorphous ratio) (Gunaratne and Hoover, 2002). Gelatinization enthalpy was significantly negatively correlated with amylose and phosphorus contents of the starches (Table 4).

Gelatinization temperature is considered reflection of the degree of orderly arrangement of molecules in the starch granule. T_o is influenced by short amylopectin branch-chains and low gelatinization temperatures are characteristic of starches with larger proportions of short amylopectin branch chains (Jane et al., 1999). T_p is an indication granular architecture (crystalline quality) and high peak temperature might be due to higher proportion of longer chains in the amylopectins as these require higher temperatures to dissociate completely than required for shorter double helices (Karim et al., 2007). Higher peak temperature for cocoyam starch compared to cassava starches suggests the presence of higher proportions of long amylopectin chains in cocoyam starch. Thus among cassava starches, Mbundumali could have higher proportion of long-chain amylopectins than the other varieties.

Retrograded starches showed lower gelatinization temperatures (T_o, T_p, and T_c) and smaller enthalpy than raw starches (Tables 2 and 3) indicating weaker starch crystallinity (Sasaki, 2005). T_o, T_p, and PHI values for retrograded cocoyam starch were significantly ($p<0.05$) higher than for cassava starches while T_c and R values were similar for all retrograded starches. Enthalpy and degree of retrogradation for cocoyam starch were significantly ($p < 0.001$) higher for cocoyam starch compared to the cassava starches suggesting rapid retrogradation for cocoyam starches. Retrogradation properties of starch paste are often related to structures of amylose and amylopectin. Higher retrogradation tendencies are attributed to crystallization involving small amylose molecules and long chain amylopectin (Peroni et al., 2006). Our results therefore suggest that cocoyam starch contain amylose and amylopectin molecules with such characteristics. Among the cassava varieties, Mbundumali, Mkondezi and Silira exhibited lower thermal properties of the retrograded starches compared to other cassava varieties.

Conclusion

Results of this study have revealed differences in chemical compositions and functional properties of the starches with crop and within varieties of the crop. Cocoyam showed small to medium polyhedral starch granules while cassava starches showed small to large rounded, irregular with oval and truncated ellipsoidal-granules. Cocoyam starch had lower amylose content but higher phosphorus content, maximum wavelength of starch-iodine complex and blue value than the cassava starches. Cocoyam starch showed lower swelling power and solubility. The gelatinization ranges for cocoyam and cassava starch were similar however cocoyam starch showed higher degree of retrogradation than cassava

starches. Starch from cocoyam starch was more opaque than cassava starch gels and paste clarity of cocoyam starch decreased significantly with storage. Starches from the different cassava varieties involved in this study differed in their properties. The differences in the functional properties of the starches from cocoyam and cassava could be attributed to different chemical compositions and structures.

ACKNOWLEDGEMENTS

This work is part of the ongoing human capacity development program in the Malawi project-Genetics and Chemistry of Root and Tuber Crops in Malawi (MW01) being supported by the International Program in Chemical Sciences-International Science Program (IPICS-ISP), Uppsala University, Sweden. We would like to thank the IPICS-ISP for the financial support towards this project.

REFERENCES

Bello-Perez LA, Contreras-Ramos SM, Jimenez-Aparicio A, Paredes-Lopez O (2000). Acetylation and Characterization of Banana (*Musa paradisiaca*) starch. Acta Cient. Venez. 51: 143-149.

Benesi IR (2005). Characterisation of Malawian cassava germplasm for diversity, starch extraction and its native and modified properties. Bloemfontein: PhD Thesis, Department of Plant Sciences, University of the Free State, South Africa.

Chakraborty M, Matkovic K, Grier DG, Jarabek EL, Berzonsky WA, McMullen, MS (2004). Physicochemical and Functional Properties of Tetraploid and Hexaploid Waxy Wheat Starch. Starch – Stärke. 56 (8): 339-347.

PY, Li PH, Huang CC, Wang CCR (2007). Changes in functional characteristics of starch during water caltrop (*Trapa Quadrispinosa* Roxb.) growth. Food Chem. 104:376-382.

Craig SAS, Maningat CC, Seib PA, Hoseney RC (1989). Starch paste clarity. Cereal Chem. 66:173-82.

Gibson TS, Solah VA, McCleary BV (1997). A Procedure to Measure Amylose in Cereal Starches and Flours with Concanavalin A. J. Cereal Sci. 25: 111-119.

Gunaratne A, Hoover R (2002). Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. Carbohydrate Poly. 49: 425-437.

Jane J, Kasemsuwan T, Chen JF (1996). Phosphorus in Rice and Other Starches. Cereal Foods World. 41(11): 827-832.

Jane J, Chen YY, Lee LF, McPherson AE, Wong KS, Radosavljevic M (1999). Effects of Amylopectin Branch Chain Length and Amylose Content on the Gelatinization and Pasting Properties of Starch. Cereal Chem. 76(5): 629-637.

Karim AA, Toon LC, Lee VP, Ong WY, Fazilah A, Noda T (2007). Effects of phosphorus contents on the gelatinization and retrogradation of potato starch. J. Food Sci . 72(2): 132-138.

Maeda T, Maryant O, Morita N (2004). Characteristics of Java Taro Starches and Physical Properties of Acid- and Heat-treated Taro Starches. J. Applied Glyco. 59(2): 109-113.

Masumbu F (2002). Production of cold-setting adhesives using starch and dextrins from cassava (Manihot esculenta Crantz). MSc in Applied Chemistry Thesis. Zomba, Malawi: University of Malawi.

Mishra S, Rai T (2006). Morphology and functional properties of corn, potato and tapioca starches. Food Hydro. 20: 557-566.

Moorthy, S. N. (2002). Physicochemical and functional properties of tropical tuber starches: A review. Starch/Starke. 54: 559-592.

Moorthy SN, Thankamma Pillai PK, Unnikrishnan M (1993). Variability in starch extarcted from taro. Carbohydrate Poly. 20(3): 169-173.

Murphy J, Riley JP (1958). A Single-Solution method for the determination of soluble phosphate in sea water. J. Mar. Biol. Ass. UK. 37: 9-14.

NSO (1999). Bill of entry on starches, dextrins and other modified starches (1994-1999). Zomba, Malawi: National Statistics office.

Pérez E, Schultz FS, de Delahaye EP. (2005). Characterization of some properties of starches isolated from *Xanthosoma sagittifolium* (tannia) and *Colocasia esculenta* (taro). Carbohydrate Poly. 60: 139-145.

Peroni F, Rocha T, Franco C (2006). Some structural and physicochmical characteristics of tuber and root starches. Food Sci. Tech. Int. 12(6): 505-513.

Riley CK, Wheatley AO, Asemota HN (2006). Isolationand characterization of starches from eight Dioscorea alata cultivars grown in Jamaica. Afri. J. Biotechnol. 5 (7): 1528-1536.

Sandhu KS, Singh N, Malhi NS (2005). Physicochemical and thermal properties of starhes separated from corn produced from crosses of two germ pools. Food Chem. 89: 541-548.

Sasaki T (2005). Effect of wheat starch characteristics on gelatinizaion, retrogradation and gelation properties: A review. JARQ. 39 (4):253-260.

Sasaki T, Masuki J (1998). Effect of wheat structure on swelling power. Cereal Chem. 75: 525-529.

Schmitz CS, de Simas KN, Joao JJ, de Mello Castanho Amboni RD, Amante ER (2006). Cassava starch functional properties by etherification-hydroxypropylation. Int. J. Food Sci. Tech. 41: 681-687.

Sefa-Dedeh S, Kofi-Agyir Sackey E (2002). Starch structure and some properties of cocoyam (*Xanthosoma sagittifolium* and *Colocasia esculenta*) starch and raphides. Food Chem. 79: 435-444.

Srichuwong S, Sunarti TC, Mishima T, Isono N, Hisamatsu M (2005). Starches from different botanical sources II: Contribution of starch structure to swelling and pasting properties. Carbohydrate Poly. 62: 25-34.

Sriroth K, Santisopasri V, Petchalanuwat C, Kuotjanawong K, Piyachomkwan K, Oates CG (1999). Cassava starch granule structure-function properties: influence of time and conditions at harvest on four cultivars of cassava starch. Carbohydrate Poly. 38: 161-170.

Tang H, Mitsunaga T, Kawamura Y (2005). Functionality of starch granules in milling fractions of normal wheat grain. Carbohydrate Poly. 59: 11-17.

Tester RF, Yusuph M, Millam S, Davies HV (2004). Effects of temperature on the physicochemical properties of starches extracted from microtubers grown from different potato cultivars. J. Sci. Food Agric. 84: 1397-1404.

Tetchi FA, Rolland-Sabate A, Amani GN, Colonna P (2007). Molecular and physicochemical characterisation of starches from yam, cocoyam, cassava, sweet potato and ginger produced in Ivory Coast. J. Sci. Food Agric. 87: 1906-1916.

Thomas DJ, Atwell WA (1999). Gelatinization, Pasting and Retrogradation. In D. J. Thomas, and W. A. Atwell, Starches: Practical guides for the food industry. St Paul, Minnesota, USA: Eagan Press. pp. 25-29.

Tziotisa A, Seetharamanb K, Klucinec JD, Keeling P, Pamela J (2005). Functional properties of starch from normal and mutant corn genotypes. Carbohydrate Poly. 61: 238-247.

Van Hung P, Morita N (2005). Physicochemical properties and enzymatic digestibility of starch from edible canna (*Canna edulis*) grown in Vietnam. Carbohydrate Poly. 61: 314-321.

Wang JK (1983). Taro. In J. Wang, Taro. Honolulu: University of Hawaii Press. p. 4