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The physicochemical properties of banana starches

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Abstract

The main objective of this study was to establish the physicochemical properties of native banana starches with particular reference to key granular and molecular characteristics. The design was targeted to provide for a comparison of landrace cultivar varieties (AAA-EA) with three hybrid varieties with particular reference to: *Gonja* (AAB), *Musa Kayinja* (ABB) and *Sukali Ndizi* (AB). Starch was extracted from the study samples using a modified sedimentation technique. All banana starches were established to be of exceptionally high purity. The determined characteristics included: amylose content using an amperometric technique, crystallinity and crystal type using X-ray diffraction characterisation, granular size using a laser beam technique, gelatinization endotherms using differential scanning calorimetry (DSC) and pasting viscosity using brabender visco amylograph. The amylose content ranged between 8 – 21%. The X-ray diffraction measurements showed no remarkable difference in the crystallite structure and although the crystallinity was unusually high for B crystals, all the banana starches conformed to the latter crystal type. The starch granule shape ranged between 6 - 60mμ in size. The DSC results showed the range for the maximum endotherm temperature (70.4 -72.8 °C). The results also indicated a relationship between molecular composition and unique cooked characteristics of the AAA-EA varieties while the high endotherm values and broad ranges concurred with the level of crystallinity obtained. The Brabender cycle curves were characterised by a two stage-swelling phenomenon, very high peak viscosities (1780 -1910 VE), low cook stability and extremely high setback (2080 –2940 VE). The physicochemical properties helped to explain the extensive shelf life of banana flours besides, rendering the banana starches potentially useful in a wide range of application in the food industry.

Key words: Amylose viscosity, characteristics, granular, *Musa* spp., X-ray diffraction

Background

Native starch physicochemical properties fall under two broad subtitles, granular and molecular characteristics. The granule size has been proved to be species specific with reference to the level of maturity. Many authors (Franco and Ciacco,1992; Sahai and Jackson,1996) have reported the impact of granule on starch physicochemical properties. The amylose concentration of normal starches of higher plants has also been established to be equally wide among species of the starch origin with the species range for amylose at 11-37% (Deatherange *et al.*, 1955). Consequent to conformation of starch macromolecules, starch has been proved to be partially amorphous and partially crystalline with percentage crystallinity ranging between 15 – 45% (Zobel *et al.*,1988). Starch granules are also broadly grouped according to distinction in diffraction patterns of X-rays as a result of the cell geometry and the amount of water in the packing of the granular cell. Cereals are generally characterised with the "A" pattern while roots, tuber and fruits have the "B" pattern. There is also a hybrid of both patterns known as the "C" pattern (Zobel, 1984; Imberty *et al.*, 1991; Zobel, 1992).

Zobel (1992) projected granular structure to partially account for starch properties including: granular density, resistance to chemical and enzymatic degradation and gelatinisation, gelation and retrogradation characteristics. Starch granule is generally insoluble in cold water but on heating in cold water starch undergoes the pasting process which was described by Meyer and Gibbon (1957) as constituting two opposing forces; i.e., the swelling of the granule, followed by the release of the exude (often amylose).

The latter phenomenon has the effect of increasing paste viscosity while at the same time breaking intra molecular forces within the granule, which affects granular integrity and subsequent paste mechanical properties. Consequently, the mechanical properties of starch gels have been reported to be influenced by the rheological characteristics of the amylose gel matrix, the volume fraction and rigidity of the gelatinised granule as well as interaction between the starch components (Eliason, 1986).

Viscosity studies using the Brabender visco amylograph have enabled the characterisation of starch from different sources or history with reference to six critical points as indicator parameters:

The pasting temperature - which registers the beginning of paste formation and is therefore a good indicator of the starch origin, modifications and additives present.

Peak viscosity - which is a measure of the maximum peak and an indicator of the beginning of the cooking stage.

Viscosity at 95°C - which is a measure of the ease of cooking of the starch.

Viscosity after a specified period of holding at 95°C - which gives a good indicator of the paste stability/ instability during cooking under relatively low shear.

Viscosity at 50°C - give a measure of the setback that occurs on cooling the hot paste.

Viscosity after holding at 50°C - gives a measure of the stability of the cooked paste under simulated use conditions (Zobel,1994).

The physicochemical properties of starches, therefore are good indicators of the potential for the starch application both in food and non-food industries for good consumer acceptability and textural properties. It is therefore, imperative to have appropriate data before undertaking processing/ modification of any starch or starchy raw material.

Data on some granular characteristics of banana starches has been generated by different researchers. Patil and Magar (1974) established physicochemical properties of banana starches from five banana varieties (3 of *M. cavendishii* and 2 of *M. paradiciaca*) which included granular and molecular characterisation but they established no varietal dependency. Kayisu *et al.* (1981) reported on the morphological and physico-chemical properties of banana (dessert variety) starch with an amylose of 16 %. Lii *et al.* (1982) reported chemical composition of an unspecified banana variety whose gelatinisation endotherm transition range was 74 - 81°C. Ling *et al.* (1982) characterised starch from *M. cavendishii* and found an amylose concentration of 19.5%. Eggleston *et al.* (1992) worked on plantain; plantain hybrids and cooking bananas and reported an amylose, content range of 9.11-17%, which concurred with work of earlier researchers. They suggested that properties of hybrid starches were ploidy level dependant and that ABB starches were more restricted in their swelling with high gelatinisation and pasting temperatures. They worked with low concentration and subsequently obtained no peaks but nonetheless recommended that banana starches could be applied in most applications, which require corn starch.

Starch studies to date have, however, not covered the triploid acuminata East African highland varieties (AAA-EA). This study, therefore, was conducted to establish the physicochemical properties of the starch of the cooking AAA-EA banana varieties and compare them to those of four hybrid varieties with particular emphasis on: *Gonja* (AAB), *Musa Kayinja* (ABB) and *Sukali Ndizi* (AB). Results would help to establish whether all banana varieties could be used as composite starches as well as help line up their corresponding potential industrial application.

Materials and methods

Sample selection

Five banana varieties were selected purposefully on basis of their genotype, local use and perceived cooked textural quality. The textural classification is based on conventional market values, which were also documented by Semwanga (1996). The samples included two AAA-EA cooking varieties (one hard and one soft, *Bukumu* (Bm) and *Nandigobe* (Nb), respectively); one dessert AB (*Sukali Ndizi (SN)*) one AAB roasting plantain (*Gonja* coded *Gj)* and one ABB juice variety (*Musa Kayinja* coded *-MK*).

Starch extraction

The starch extraction procedure followed by Eggleston *et al.* (1992) was modified to suit the requirements of the different varieties as follows:

The bananas were peeled, sliced and thereafter cooking varieties were extracted using 0.045M NaOH and blended for 35 sec. The non-cooking varieties were extracted with 0.065M NaOH and blended for 45 sec. The mashes were then filtered through a muslin cloth to separate the starch, which was washed (3-5 times) and centrifuged before drying.

Starch composition

The proximate composition of starch with respect to moisture content , starch, protein and ash content was determined to help estimate the purity of the starches using standard analytical procedures.

Amylose determination

The amylose determination was based on amperometric adaptation of the dead stop titration technique, which was modified to suit the Titro Processor 670. The principle of the method is that first reported by Larsson *et al.* (1953).

X- ray diffraction characterisation

The x-ray examinations were carried out using a technique of the Fraunhoffer Institute (IAP) Germany. The tests were done using a Siemens' Diffraktometer D5000 in symmetrical transmission using a Ge-Primary monochromator. The resultant diffraction curves were interpreted using Programmes WAXS 7 which is based on Ruland – Vonk's method to establish the percentage chrystallinity (Xc %) and the disorder value (a measure of the lattice disturbance in the crystallite). After a peak separation in the corrected diffraction curves, the mean lateral crystallite size (Dhkl) was determined.

Determination of size

Particle size distribution was determined using a Laser beam system, Mastersizer of the Malvin Instruments Ltd.(U.K) version 2.15. The system details were: Range lens 300RF mm; beam length 2.40mm; sampler MS17, Obscuration 26.6%.

Gelatinisation endotherms

The changes in the endotherm values were monitored using a Direct Scanning Calorimeter (DSC) 120,220 Seiko Instruments (Japan) calorimeter module which was integrated to a pesonal computer and printer through a Disk station. Starch slurries in a ratio of 1:5 were prepared in Al / Ag pans which were hermetically sealed and measured against water as standard. The temperature regime was between 10° C to 106°C and the heating rate was 1 K min^{-1}. The cooling at the end of each endotherm measurement was through ice. The endotherm values were calculated manually to establish peak temperature (Tp), temperature at the beginning of gelatinization (Tb), temperature at the end (Te) and enthalpy value (ΔH).

Viscosity measurements

The viscosity was measured using Brabender Visco/Amylograph following standard procedures as outlined by Haase *et al.* (1995). The starch concentration for peak formation was, however, 8.6% for the Brabender technique.

Results and discussion

Starch composition

The starch extracted from the different varieties using the procedure outlined above yielded starch which was exceptionally pure (97 - 100%) (Table 1). The protein content was within a range of values obtained by Lii *et al.* (1982) but these authors obtained lower values for ash content. Eggleston *et al.* (1992), however, obtained higher values for both protein and ash content.

Granular characteristics

Particle size range lay within the maximum range of 6-60 mμ which has been quoted by different authors for starches from different banana varieties (Shantha and Siddappa, 1970, Patil and Magar, 1974, Lii, *et al.*, 1982, Eggleston *et al.*, 1992). In contrast to other starches which have been measured using similar techniques, the median granular size of the study samples lay between that of the big wheat granules (19 mμ) and potato (41 mμ) (Seidemstücker and Fritz, 1997). The percentage crystallinity measurements showed no remarkable difference in the crystallite structure, but, the lateral crystallite size and crystallinity of sample 6-ABB were somewhat smaller. All the banana samples belonged to the B crystal type. The crystallinity was, however, appreciably lower in MK-ABB (Table 2). The crystallinity values were closer to the range of cereal starches which are A-crystal types (Zobel, 1984). The amylose content of the banana starches in this study was generally low. This concurs with Eggleston *et al.*,(1992) earlier report on banana starches. The data can be segregated along genotype lines whereby the hybrid varieties (non-cooking) presented higher levels of amylose.

Table 1. Banana starch composition.

**Sample	M.C %	Starch%	Protein%	Fat %	Ash %
Gj-AAB	10.7	98.6	0.1	Tr.	0.1
Bu-AAA-EA	11.2	98	0.1	Tr.	0.1
Nb-AAA-EA	11.3	99.7	0.2	Tr.	0.1
MK-ABB	10.8	97.4	0.1	Tr.	0.1
SN-AB	11.1	100	0.1	Tr.	0.1

All the data in Table 1 are means of two determinations. Starch , protein, fat and ash are determined on dry basis.

The gelatinization endotherms lay within close range of those reported by Patil and Magar (1974) for an unspecified variety and Lii *et al.* (1982) for Cavendish. They were, however, appreciably higher than those obtained for Plantain Bobby, Plantain hybrid and Bluggoe by Eggleston *et al.*(1992). T_{max} had a positive correlation to granule average particle size of r = 0.5 which agreed with the observation of Sahai and Jackson (1996) that larger granules with low crystallinity were more susceptible to heat. On the contrary *Nandigobe* (AAA-EA) which had the lo:vest mean particle size also had a relatively lower T_{max}

The granular characteristics on the whole showed no clear genotype or functional segregation. The X-ray diffraction data, however, tended towards the higher range (cf. potato 24%) which supports the low amylose/amylopectin ratios. The gelatinization endotherms did not show genotypic dependency but were generally high which concurred with the level of crystallinity obtained.

Pasting viscosity

Table 3 shows the results of the Brabender visco amylograph, which is a low shear. These banana starches like that studied by Kayisu (1980) did not produce peaks at concentration under 6% (s/w) which agree with the highly restricted swelling typical of the banana starches. The above results were obtained at a concentration of 8.6% (s/w) and they showed two types of swelling characteristics. Gj-AAB displayed rapid swelling but with a flat peak (Fig. 1) while the other three samples showed rapid swelling within the first few minutes of the pasting cycle. This was followed by a phase of restricted swelling of varying length commencing around 85°C which ended in sharp peaks (Fig.1). The latter behaviour is indicative of a two - stage swelling mechanism similar to that of milo starch (Leach *et al.*, 1959). However, in the case of banana starch the rapid swelling period precedes the restricted swelling. Leach *et al.* (1959) attributed the behaviour of milo starch to two sets of bonding forces within the starch granule relaxing at different temperature levels.

The high sharp peaks were accompanied by pronounced thinning on cooking for 30 minutes as evidenced by the initial and final viscosity at 92°C (Fig. 1 and Table 3). The thinning effect is indicative

Table 2 Granule particle size and X-ray diffraction measurements of bananas starches.

Sample	Particle (median) _ d mμ		Xc %	K -10^2 (nm)	Dhkl (nm)			Crystal type
	size	Range			D_{100}	D_{120}	D_{300}	
Gj - AAB	24.05	10.06-45.47	2.25	9.4	7.2	6.6	B	B
Bu-AAA-EA	22.25	8.27- 38.3	ND	ND	ND	ND	ND	ND
Nb - AAA-EA	19.67	6.42-35.19	2.39	9.1	8.5	7.1	B	B
MK - ABB	25.8	14-08-38.18	2.24	8.5	6.8	6.8	B	B
SN -AB	24.1	9.42-41.36	2.54	9.2	7.9	7.2	B	B

Xc =Chrystallinity, K = radom parameter, Dhkl = mean lateral Crystallinity values Dhkl .

TABLE 3. Banana starch granular and pasting characteristics.

Sample/ genotype	Amylose %	Gelatinisation					Amylograph Data VE			
		ΔH mJ/mg	T_{max}	T_{begin}	T_{end}	Trange	Peak max	Peakmin hold	Difference Peak- (max-min)	Peak-max after hold 50°C
Gj-AAB	19.19	12.30	70.40	66.35	76.45	10.1	1910	840	1070	2260
Bu-AAA-EA	12.94	13.20	71.25	66.75	78.05	11.3	-	-	-	-
Nb-AAA-EA	8.44	11.10	70.90	65.90	76.58	10.68	1885	910	975	2080
MK-ABB	15.49	11.05	72.5	68.00	77.28	9.28	1780	1080	700	2775
SN-AB	20.59	11.45	72.75	67.50	78.60	11.1	1870	1125	745	2940

of progressive fragmentation and solubilisation of the starch granule and therefore, a measure of cook/shear stability. The flattening of the peak of sample Gj-AAB is most likely a direct consequence of mechanical breakdown of the excessively swollen granule at this point. The percentage remaining viscosity at the end of the 30 min cook period at 92°C was 44% for Gj-AAB, 48% for Nb-AAA-EA, 60 % for SN-AB and 61% for MK-ABB. Consequently 2-AAB and 5-AAA-EA were less cook-stable, whereas samples 8-AB and 6-ABB showed only moderate thinning. At concentrations of 6% or below, however, all the banana starches have been reported to display remarkable stability to cooking with some increases in viscosity on cooking (Kayisu, 1980; Eggleston *et al.* 1992). The swelling and thinning of the paste, therefore, appear to have a high concentration dependency under low shear.

The extent of increase in viscosity at 50°C has been said to reflect the retrogradation tendency of the starch product (Mazurs *et al.*, 1957). The setback was extremely high for all the banana starches with no parallel from common native starches but perhaps only comparable to that of acid modified corn starch (Mazurus *et.al* 1957). The higher restriction to swelling of the banana varieties enabled use of high starch concentrations for pasting studies which appear to enhance the associations of molecules on cooling. The setback was more dependent on the cook/shear stability ($r = 0.9$) than on the amylose content ($r = 0.6$). In other words the effect on starch pastes of increasing starch concentration may be relative to that of using a higher amylose starch which for the same variety is only attainable through breeding.

Conclusion

The banana starches level of purity especially with respect to fat would make them generally favourable for making gum confections (Osman, 1965). The high gelatinisation temperature favours application of simple hybrid dryers without apparent loss of product quality. The low level of amylose in the cooking variety may apparently favour its soft texture as waxy starches generally have poor

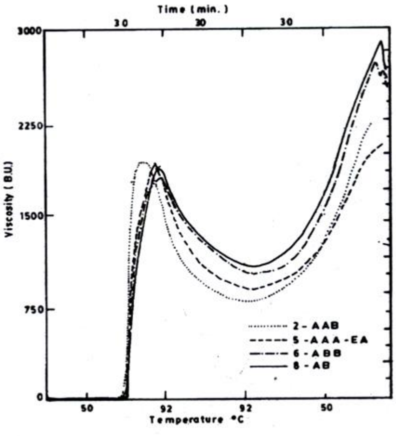

Figure 1. Brabender viscoamylograph for four banana starches.

retrogradation properties. The starches from the soft cooking banana therefore, most likely would have good thaw stability which would make it good for thickening sauces and confectioneries that require cold storage cycles. The banana high restricted swelling which necessitated the higher concentrations (>6%) to producing peak viscosity would favour the use of all the banana starches in the study with exception of Gj-AAB in similar applications that require wheat or corn starch such as replacement of wheat flour in fine bakery products. The restricted swelling also would favour: application of banana starch as a diluent in powders, the extremely long shelf-life of banana flours and chips, incorporation of higher amounts of flour in porridges/soups targeting protein energy malnutrition disorders. The restriction to swelling may also contribute to shelf stability of banana flours and may favour the incorporation of banana starches in the manufacture of biodegradable plastic where normally corn and rice starch have been used.

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