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Isolation, chemical modification and physicochemical characterisation of Bambarra groundnut (*Voandzeia subterranean*) starch and flour

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Abstract

The proximate and physico chemical characterisation of Bambarra groundnut (*Voandzeia subterreanea*) flour and starch was studied. Oxidation and acetylation of the native starch reduced the percentage ash, crude protein, crude fibre, and crude fat. The swelling capacity increased with increase in temperature for both starch and flour; the acetylated starch, however, showed the highest swelling power. There is increased swelling and solubility in the alkaline region. Oxidized starch had the highest oil and water absorption capacity (3.04 and 2.40 g/g, respectively). The least gelation concentration for the starches ranged from 6 to 10% (w/v), while the alkaline water retention increased when the starches were blended with wheat flour, with the blends of wheat flour and acetylated starch giving the best result. Brabender viscographic studies showed lowering of pasting temperature after oxidation and acetylation, with oxidised starch showing the lowest pasting temperature. Both oxidation and acetylation lowered the peak viscosity (P_V), hot paste viscosity (H_v) and cold paste viscosity (C_v). Chemical modification enhanced the stability of the starches with oxidised starch having the highest stability value, followed by acetylated starch.

Keywords: Bambara groundnut; Oxidized starch; Acetylated starch

1. Introduction

Legume seeds are of prime importance in human and animal nutrition, in tropical Africa, especially Nigeria. This is due to their high protein content (20–50%), which in general is well above twice the level found in cereal grains and significantly more than the level in conventional root crops (Ustimenko-Bakumovsky, 1983). The chemical compositions of some of these legumes, e.g. cowpea (*Vigna unguiculata*), soya bean (*glycine* max) groundnut (*arachis hypogea*), have been studied (Oates, 1990).

There are some legumes, however, that are lesser known and under-utilized outside their indigenous areas. A monograph was published highlighting the potential of some little-known but promising tropical legumes (NAS, 1984).

Bambarra groundnut (*Voandzeia subterranean*) is one of the under-utilized legumes in Nigeria. Numerous studies have been carried out on the chemical composition and nutritional properties of its seeds (Adjetey & Sey, 1998; Barimalaa & Auoghalu, 1997; Enwere & Hung, 1996; Odeigah & Osanyinpeju, 1998). Obizogba (1990) reported that blends of Bambarra groundnut showed nutritional superiority to other blends of legumes studied. However, there is little information on the isolation and characterization of Bambarra groundnut starch.

The objective of the present study was, therefore, to isolate and characterize the starches of Bambarra groundnut (*Voandzeia subterranean* L.). The isolated starch was further derivatized by acetylation and oxidation. The studies carried out on characterization of the starches include: evaluating the proximate composition of the dehulled seeds and their starches, and determining their physico chemical properties, such as swelling, solubility, alkaline water retention, oil and water absorption, gelation and pasting characteristics.

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It is hoped that the data generated from the studies may be useful for the industrial utilization of the starch.

2. Materials and methods

2.1. Flour preparation

Bambarra groundnut was purchased at Bodija market, Ibadan, Oyo State, Nigeria. The seeds were screened to eliminate the defective ones. Water was added to the samples and left overnight. The seeds were manually dehulled, dried in an oven at 45 °C, then dry-milled to a fine powder. The flour was stored in polythene bags and kept in a refrigerator at 4 °C prior to use.

2.2. Starch isolation

The method of Sathe, Desphande, and Salunkhe (1982) was employed, with modifications, for the starch isolation. Occasional stirring was provided during all extractions. The extraction procedure is presented in Fig. 1.

2.3. Modification of the legume starch

Acetylated and oxidized legume starches were prepared by a method originally employed by Sathe and Salunkhe (1981b).

2.4. Proximate analysis

Moisture content, ash, crude fibre, crude protein, and fat were determined by AOAC methods (1990).

The pH of a 20% (w/v) sample of slurry was determined using an Omega HPPX digital pH-meter. The carbohydrate content was determined by difference.

The determination of degree of substitution of the acetylated starch was carried out as described by Smith (1967), while the method of Parovuori, Hamunen, Forsell, Autio, and Powanen (1995) was employed for the determination of degree of substitution of oxidized starch (carboxyl content).

2.5. Effect of temperature on solubility and swelling

A starch sample (1.0 g) was accurately weighed and quantitatively transferred into a clear dried test tube and re-weighed (W_1). The starch was then dispersed in 50 cm^3 of distilled water using a blender.

The resultant slurry was heated at the desired temperature; 65, 75, 85 or 95 °C) for 30 min in a water bath. The mixture was cooled to 30 ± 2 °C and centrifuged (500 rpm, 15 min).

Aliquots (5 ml) of the supernatant were dried to a constant weight at 110 °C. The residue obtained after drying the supernatant represented the amount of starch solubilised in water. Solubility was calculated as g per 100 g of starch on a dry weight basis.

The residue obtained from the above experiment (after centrifugation) with the water it retained was quantitatively transferred to the clean dried test tube used earlier and weighed (W_2).

$$\text{Swelling of starch} = W_2 - W_1/\textit{weight of starch}$$

2.6. Effect of pH on swelling and solubility

To determine the effect of pH on swelling and solubility of the starch, slurries (1%, w/v) were prepared in distilled water and the pH adjusted to the desired values with 0.1M HCl or 0.1M NaOH. The slurries were then allowed to stand at 30 ± 2 °C for an additional 30 min, centrifuged (5000 rpm, 15 min) and the swelling (1%) and solubility determined as described above.

2.7. Oil and water absorption capacities

The method of Beuchat (1977) was employed to determine the oil and water absorption capacities of the starch.

2.8. Gelation studies

The gelation properties of the starch were determined as described by Sathe and Salunkhe (1981a).

2.9. Alkaline water retention

Blends of composite flour containing 0, 10, 20, 30, 40, 50 and 100% of the samples and wheat flour on a replacement basis, were prepared. Each blend (1.0g) was quantitatively placed in a test-tube (test tube weighed with dry sample W_1), 5.0ml of 0.1M $NaHCO_3$ was added and mixed for 30s in a Variwhirl mixer. The samples were then allowed to stand at 30 ± 2 °C for 20 min, centrifuged (200 rpm, 15 min) and drained for 10 min at an angle 10–15 ° to the horizontal. Test tubes with their contents were then weighed (W_2) and the alkaline water retention calculated as follows:

$$\text{Alkaline water retention capacity (g/g) of sample} = W_2 - W_1$$

2.10. Brabender viscography

The Brabender viscographic studies of 8% starch paste (36 g of starch on dry weight basis in 450 ml or water) were carried out in a Brabender viscoamylograph (Type 801203 W.G), equipped with a 700 cmg sensitivity cartridge. The starch paste was heated from 30 to 95 °C, kept at this temperature for 30 min, then cooled to 50 °C. The viscosity was recorded at a constant rotational velocity of the measuring vessel, fixed at 75 rpm, and heating, as well as the cooling rate, was 1.5 °C/min throughout the range of gelatinization, holding and cooling steps.

The pasting temperature (T_v), peak viscosity (P_v), hot paste viscosity (H_v), cold paste viscosity (C_v), stability (ST) and setback value (SB) were recorded.

3. Results and discussion

3.1. Proximate composition and yield

The amount of starch recovered from the legume flour was 37.50% (Table 1). This is considerably lower than that obtained for Enset starch, which is about 90% (Gebre-Mariam & Schmidt, 1996) The starch contents of fieldpeas and horsebeans, as reported by Vose (1980), were 44 and 48%, respectively. The moisture content of

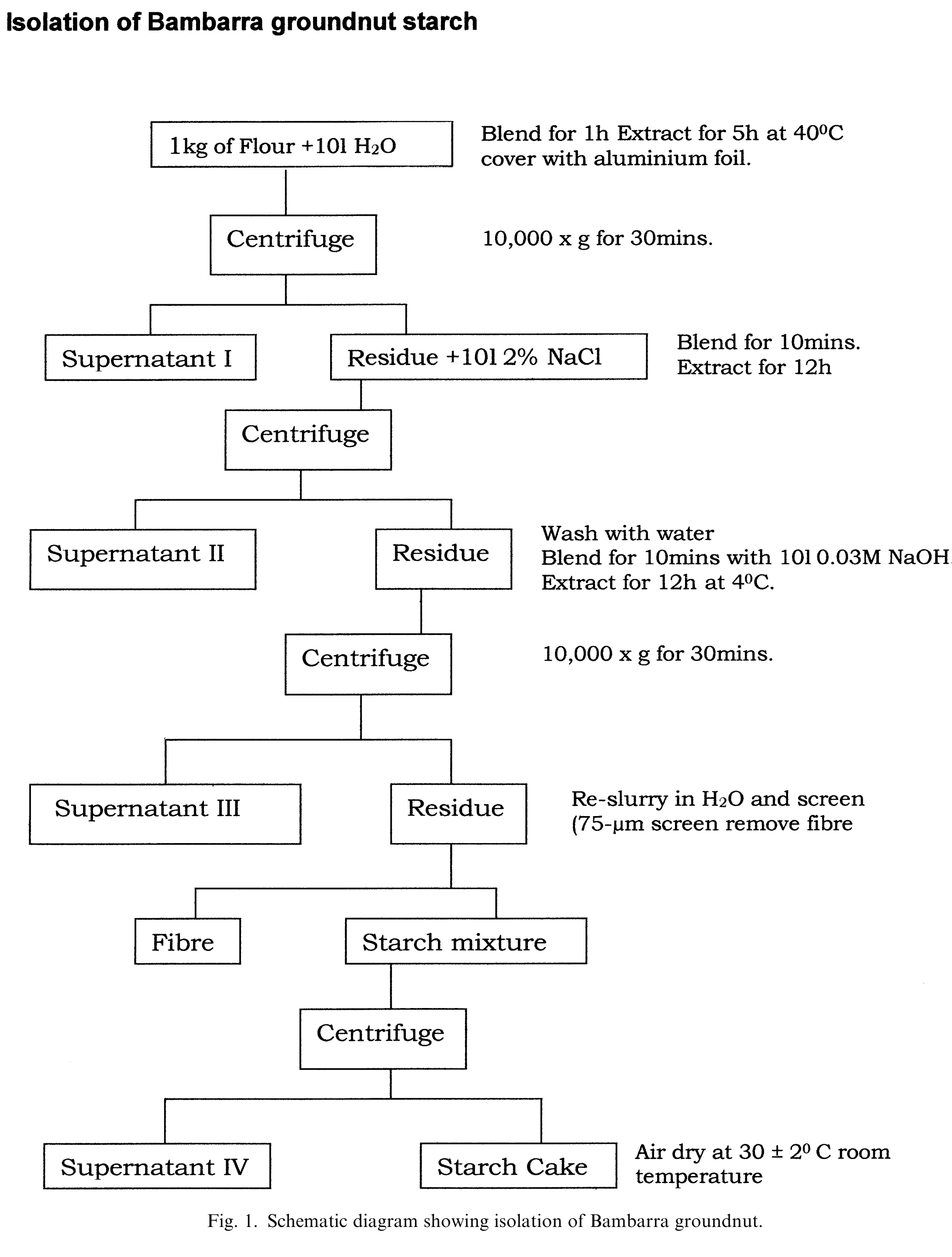

Fig. 1. Schematic diagram showing isolation of Bambarra groundnut.

Bambarra starch ranged between 9.15 and 14.80%. The moisture content of starch depends to a large extent on the method employed in drying (Shieldneck & Smith, 1971). Moisture modifies the flow and mechanical properties of many powders, including starches (Pilpel, 1971).

The values of the percentage protein, crude fibre, crude fat and ash are low for the starch relative to bean flour (Table 1). This indicates that the starches are pure. Modification of the native starch by acetylation and oxidation further reduces the percentage protein, crude fibre, crude fat and ash. This is probably due to further screening and washing during the preparation of the modified starches

3.2. Swelling

The effect of temperature on swelling power of Bambarra flour and starch (Table 2) reveals that each type of starch swells differently, indicating differences in the molecular organization within the granules. However, the swelling power of starch and flour increases with temperature.

The degree of swelling and the amount soluble depends on the starch species (Schoch, 1964). It has been proposed that bonding forces within the granules of starch affect swelling power. Consequently, highly associated starch granules, with an extensive and strongly bonded micellar structure, should display relatively greater resistance to swelling (Leach, McCowen, & Schoch, 1950).

The swelling power of acetylated bambarra starch, at all temperatures, was much higher than purified bambarra starch, which is in turn, higher than oxidized starch (Table 2). This indicates that oxidation reduces the swelling power while acetylation increased it. Hypochlorite oxidation is a highly effective means for weakening the internal structure of starch granules, thereby making starch more soluble, but with much reduced power to swell.

There was substantially higher swelling power between 75 and 95 °C for native starch of bambarra. Schoch and Maywald (1968) observed similar increases for Lima-bean starch. To account for a two-stage swelling of corn starch, it has been speculated that the granules are held together by two sets of bonding forces, a weak association relaxing at 65 to 75 °C, and a second and stronger association, relaxing at 85–100 °C. By similar reasoning, the granules of Bambarra might be considered as internally associated only by relatively strong bonding forces.

The effect of pH on the swelling power of Bambarra flour and its starches (native and modified) (Table 2) shows that there is little change in the swelling power of flour at either alkaline or acidic pH. However, there is increased swelling for all the starches (native and modified) in the alkaline region (pH 8–10), while there is very little increase in the acidic region (pH 2–6). This behaviour could be due to the interaction between the protein and starch at alkaline pH, when both starch and protein have negative charges as against acidic pH at when proteins bear a positive charge (Shieldneck & Smith, 1971) Percentage swelling is therefore expected to be high at alkaline pH and low at acidic pH, depending on the amount of protein associated with the starch.

3.3. Solubility

The solubility of all the starches increased with temperature (Table 3); however, modification (by acetylation and oxidation), increased the solubility of

Table 1
Proximate composition of Bambara flour and its starches (native and modified)[a]

Sample	BGF	BNS	BOS[b]	BAS[c]
Starch yield (%)	–	37.50[d]	92.50[e]	89.25[e]
Protein (%)	20.7±0.02	1.00±0.08	0.75±0.01	0.63±0.01
Ash (%)	0.63±0.02	0.04±0.01	ND	ND
Crude Fibre (%)	0.83±0.03	ND	ND	ND
Crude Fat (%)	1.24±0.01	0.08±0.02	ND	ND
Moisture (%)	9.50±0.02	14.80±0.01	9.15±0.05	12.10±0.12
Carbohydrate (%)	67.1	84.1	90.1	87.3
pH	6.38±0.12	6.50±0.51	7.69±0.11	6.10±0.18

[a] BGF, Bambara groundnut flour; BNS, Bambara native starch; BAS, Bambara acetylated starch; BOS, Bambara Oxidized Starch, ND, not detected. Results are means of duplicate determination.
[b] Degree of substitution = 0.32.
[c] Degree of substitution = 0.35.
[d] On flour basis.
[e] On native starch basis.

Table 2
Effect of temperature on swelling of Bambarra groundnut flour and its starches (native and modified)[a]

Swelling power	BGF (%)	BOS (%)	BAS (%)	BNS (%)
65 °C	259.40	126.30	156.90	138.50
75 °C	443.50	210.30	305.50	249.30
85 °C	713.20	390.90	515.40	456.90
95 °C	749.50	452.90	602.05	498.70

[a] BGF, Bambara groundnut flour; BNS, Bambara native starch; BAS, Bambara acetylated starch; BOS, Bambara oxidized starch.

Table 3
Effect of temperature on solubility of Bambarra groundnut flour and its starches (native and modified)[a]

Swelling power	BGF (%)	BOS (%)	BAS (%)	BNS (%)
65 °C	5.20	2.90	2.50	2.70
75 °C	7.90	8.70	4.80	6.50
85 °C	12.85	10.50	8.90	9.40
95 °C	18.00	16.70	12.50	14.50

[a] BGF, Bambara groundnut flour; BNS, Bambara native starch; BAS, Bambara acetylated starch; BOS, Bambara oxidized starch.

bambarra starch relative to its native starch. The oxidized starch showed the highest solubility. This is probably due to the weakening of the starch granules during hypochlorite oxidation, leading to improved solubility (Shieldneck & Smith, 1971). The solubility characteristics of acetylated bambarra starch are mainly dependent upon the degree of substitution and polymerisation (Krucer & Rutenberg, 1976). There was little effect on the solubility of the bean flour at either alkaline or acidic pH. However, solubility of the modified Bambarra starches (oxidized and acetylated) was greater than that of the native starch of bambarra in the alkaline regions, while their solubilities were less than that of unmodified starch of bambarra in the acidic regions. The increased solubility at alkaline pH may be due to increased hydrophilic character of the starch at these pH values.

The solubility of native and oxidized bambarra starches exhibited a maximum at pH 4.0, while that of acetylated bambarra exhibited a minimum at pH 6.0. Oxidized bambarra starch would find good applications in acidic and basic food items.

3.4. Oil and water absorption

The bean flour had the highest water absorption capacity 2.60 g/g (Table 4). This was higher than that of Great Northern bean, reported by Sathe and Salunkhe (1981a, 1981b), and succinylated peanut flour, reported by Beuchat (1977). Oxidation of Bambarra starch favours water and oil absorption capacity.

Table 4
Oil and water absorption capacities of Bambara groundnut flour and its starches (native and modified)

Sample[a]	Water absorbed (g/g)	Oil absorbed (g/g)
BGF	2.60±0.04	1.96±0.10
BNS	2.00±0.10	1.76±0.10
BAS	2.10±0.02	2.55±0.21
BOS	2.40±0.01	3.04±0.18

[a] BGF, Bambara groundnut flour; BNS, Bambara native starch; BAS, Bambara acetylated starch; BOS, Bambara oxidized starch.

3.5. Gelation

The least gelaton concentrations for the native, oxidized, and acetylated, bambarra starches were 8, 10 and 6% (all w/v), respectively, (Table 5) while the bambarra flour does not form a gel up to 14% (w/v) concentration. Akintayo (1998) reported similar values for African yambean, lima bean and pigeon pea starches.

3.6. Alkaline water retention

Alkaline water retention capacity is a parameter that is related to cookie diameter (Yamzaki, Donelson, & Kwolek, 1977).

The results of alkaline water retention capacities (Table 6) show that, replacing the wheat flour by the starch, resulted in increased alkaline water retention for all the starch. Rasper and Deman (1980) reported increased water retention capacity of wheat flour–starch blends. They partially attributed this increase in water absorption to the surface area of the starch phase and excessive dilution, at high concentration of starch, of the continuous phase.

Sathe and Salunkhe (1981a, 1981b) suggested that, in addition to these factors, the water absorption may also have an important role in water retention by wheat flour–starch blends. The present results indicate that Bambarra groundnut flour and the modified and unmodified starches could serve as an extension of wheat flour in cookie-making.

3.7. Pasting characteristics

The pasting characteristics of unmodified and modified Bambarra groundnut starches are presented in Table 7. Oxidation and acetylation reduced the gelatinization temperature of the starch due to weakening or scission of the D-glucosidic bonds during the processes of modification (Kruser & Rutenberg, 1976).

Table 5
Gelation capacity of Bambarra flour and its starches (native and modified)[a]

Sample conc. (% w/v)	BGF Gelation	State	BNS Gelation	State	BOS Gelation	State	BAS Gelation	State
2	–	Liquid	–	Liquid	–	Liquid	–	Viscous
4	–	Liquid	–	Viscous	–	Liquid	–	Viscous
6	–	Liquid	–	Viscous	–	Viscous	+	Gel (LGC
8	–	Liquid	+	Gel (LGC)	–	Viscous	+	Gel
10	–	Viscous	+	Firm gel	+	Gel (LGC)	+	Firm gel
12	–	Viscous	+	Very firm gel	+	Gel	+	Firm gel
14	–	Viscous	+	Very firm gel	+	Firm gel	+	Very firm gel

[a] BGF, Bambara groundnut flour; BNS, Bambara native starch; BAS, Bambara acetylated starch; BOS, Bambara oxidized starch; LGC, Least gelation concentration.

Table 6
Alkaline water retention capacities of wheat flour/bambarra bean starches (and modified) blends[a]

Wheat flour replacement (%)	Alkaline water retention capacity (g/g) of			
	BGF	BNS	BOS	BAS
0	1.33±0.42	1.28±0.64	0.92±0.75	1.04±0.18
10	0.76±0.31	0.82±0.89	0.78±0.42	0.55±0.21
20	0.80±0.82	0.87±0.10	0.84±0.53	0.68±0.11
30	0.82±0.22	0.89±0.69	0.95±0.64	0.72±0.32
40	0.84±0.57	0.93±0.63	1.05±0.72	0.77±0.43
50	0.89±0.82	0.98±0.40	1.75±0.81	0.83±0.42
100	1.48±0.35	1.47±0.91	1.40±0.31	1.46±0.22

[a] BGF, Bambara groundnut flour; BNS, Bambara native starch; BAS, Bambara acetylated starch; BOS, Bambara oxidized starch; Results are means of duplicate determination.

Table 7
Pasting characteristics of unmodified and modified Bambara groundnut starches showing pasting temperature (Tp), peak viscosity (P_v),Hot paste viscosity (H_v), cold paste viscosity (C_v), stability (ST) and setback (SB) at 8% w/w concentration[a]

Parameter	BNS	BOS	BAS
Tp (°C)	84	73	75
P_v (BU)	790	720	740
H_v (BU)	710	550	640
C_v (BU)	2000	1500	1750
ST[b] (BU)	80	170	100
SB[c] (BU)	1210	780	1010

[a] BNS, Bambara native starch; BOS, Bambara oxidised starch; BAS, Bambara acetylated starch.
[b] $P_v - H_v$ after 30 mins holding at 95 °C.
[c] $C_v - P_v$.

The peak viscosity (P_v) at any concentration is an important distinguishing feature of a starch. The bambarra native starch shows a peak viscosity higher than those of the acetylated and oxidised starch, attributed to unrestricted swelling of the starch, due to lack of substituent functional groups. The viscosity values obtained after the isothermal holding at 95 °C (H_v) were generally lower than the peak viscosity value. Considerable increase in cold paste viscosity (C_v), seen in all the starches, is the result of the association of colloidally dispersed or dissolved starch molecules into larger units as the solutions are cooled. However, oxidised and acetylated starches show lower values because the hydroxyl group, which is the principal factor for this association, has been substituted (Gebre-Mariam & Schmidt, 1996). Oxidised bambarra starch shows the highest value of stability (ST) and lowest setback value (SB), followed by acetylated bambarra starch, with the native starch showing the lowest stability value and a high setback value, because the tendency toward setback or gel formation has been minimised in the substituted starches, due to the presence of functional groups which prevent the starch chains from associating. Another reason could be partial depolymerisation that has occurred during the processes of modification.

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