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SYNTHESIS, PHYSICOCHEMICAL CHARACTERIZATION, AND FUNCTIONAL PROPERTIES OF AN ESTERIFIED STARCH FROM AN UNDERUTILIZED SOURCE IN NIGERIA

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ABSTRACT

Acha *(Digitaria exilis* Stapf), also known as Findi, Hungry rice, Petit mil and White fonio, is a small seeded cereal, indigenous to West Africa, which is generally classified as millet. It grows in various parts of Nigeria, Sierra Leone, Ghana, Guinea Bissau and Benin Republic. That species is the most important of a diverse group of wild and domesticated *Digitaria* species that are harvested in the savannas of West Africa. It is one of the primary cereals of southern Sudan and Ethiopia in Africa. It has potential to improve human nutrition, boost food security, foster rural development and support sustainable use of lands. In this study, acha starch was subjected to modification by acetylation. The acetylated acha starch with degree of modification 0.78 had reduced foaming capacity and amylose contents. The starches have similar organoleptic properties ranging from white, gritty, non sticky to bland tastes. Physicochemical indices investigated such as true density, bulk and tapped densities, water absorption capacity, moisture content, total and acid insoluble ash, and pH were reduced by the acetylation of acha starch. The modification resulted in a significant ($P < 0.05$) increase in the solubility as well as water and oil absorption capacities of the starch. Scanning electron microscopy revealed starch granules that were predominantly polygonal in shape. Acetylation did not alter the granule morphology. X-ray pattern of the native starch was A type, with similar pattern in the acetylated derivative. Fourier transform infrared spectroscopy (FTIR) results revealed a new band at 1728 cm-1. Thermogravimetry revealed 3 phase decomposition of both the native and modified starches. The acetylation as revealed by Differential scanning calorimetry studies improved the gelation capacity of the native starch and revealed two endothermic peaks and one exothermic peak each for both starches. There was considerable reduction in the peak temperature of gelatinization (Tp) of native starch and a significant ($P < 0.05$) decrease in the enthalpy of gelatinization (DH) was noticed after acetylation.

Key words: *Digitalis exilis*, starch, acetylation, physicochemical properties

INTRODUCTION

Fonio *(Digitaria exilis* Stapf), also known as Acha, Findi, Hungry rice and Petit mil, is a small seeded cereal, indigenous to West Africa, which is generally classified amongst the millets [1]. Fonio is grown in various parts of Nigeria, Sierra Leone, Ghana, Guinea Bissau and Benin Republic on poor sandy soils which could not sustain the growth of other, more demanding cereals. The 1000-kernel weight of fonio determined by Jideani and Akingbala [2] indicates that acha is one of the smallest cereal grain. The decorticated seeds of fonio are a staple food in some restricted areas in Africa. They are consumed mostly whole, but they are also milled into flour and they constitute a versatile raw material, which can be processed into a variety of preparations such as gruels, porridges and beverages [2]. Fonio starch has good disintegrant and binding properties [3, 4], and possesses good glidant properties [5]. It has continued to be important locally because it is both nutritious and one of the world's fastest growing cereals, reaching maturity in as little as six to eight weeks. It is a crop that can be relied on in semi-arid areas with poor soils, where rains are brief and unreliable. The grains are used in porridge and couscous, for bread, and for beer. Nevertheless, there is neither a comprehensive physicochemical characterization of fonio starch other than the limited characterization of starch obtained from two varieties of fonio [1,2] , nor is there a report on an esterified fonio starch. Starch is an inexpensive, abundant carbohydrate available from many plants. A large percentage of starches are from crops that serve as sources of staple foods. This development has necessitated research on alternative means of sourcing starch for domestic and industrial uses. Focus on underutilized plant resources for starch production has stimulated research on crops such as mucuna beans [6, 7], bambarra groundnut [8, 9], new cocoyam [10], black Gram [11], Great Northern Bean [12], sago [13], pigeon pea [14], yam bean [15], field pea [16], lentil [17], Tiger nuts [18], Tacca tubers [19, 20] and jack bean [21]. These plants differ in their physical and chemical properties, resulting from the difference in their molecular structure and in the morphology of their starch granules, and consequently their applications. Native starches irrespective of their source are undesirable for many applications, because of their inability to withstand processing conditions such as extreme temperature, diverse pH, high shear rate, and freeze thaw variation [20]. To overcome this challenge, modifications are usually done to enhance or repress the inherent property of these native starches or to impart new properties to meet the requirements for specific applications [21]. Modified starches have found useful application in the pharmaceutical, food, paper and textile industries as binders, disintegrants, fillers, emulsion stabilizers and adhesives (7 – 9, 21)

Various methods of starch modification include physical, chemical, enzymic and biological processes. Among these methods, chemical means is the most frequently used. The significance of various modifications on starches of different origins has been expounded in the literature [6 – 8, 21 – 25]. These modifications are carried out to improve the functional and physicochemical parameters of the starches in various industries, particularly where native starch itself cannot give optimal performance. Previously, many types of chemical modifications have been applied to starches of various plant sources. These include acid hydrolysis, oxidation, etherification,

esterification and cross-linking (26 – 29). Specific chemical modifications are applied to starches to meet the requirements of various industrial applications [26 – 29].

Acetylating starch has been reported to decrease its gelatinization temperature, increase its translucency, viscosity, freeze– thaw stability and reduce retrogradation [29]. Acetylation depends upon factors such as reactant concentration, reaction time, pH and presence of catalyst [29, 30], which determines the number of acetyl groups incorporated into the molecule.

The aim of the work reported herein was to undertake a comprehensive investigation of the starch obtained from *Digitalis exilis*, secondly, to chemically modify the starch by acetylation and investigate the effect of the acetylation on the physicochemical and functional properties of the starch.

MATERIALS AND METHODS

Isolation of starch and purification of native acha starch (NAS)

Good quality *D. exilis* grains devoid of defects were purchased from a local market in FCT, Abuja, Nigeria.

The method of Kunle *et al* [19] was used with some modifications. *Two kg of* winnowed *D. exilis* grains were steeped in 10L of 0.075 % w/v aq sodium metabisulfite for 24 h at 28 ^{o}C, after which the steeping solution was discarded, and the swollen grains washed with water. The sample was then blended using a blender (Braun, Germany). The slurry obtained was resuspended in 5 L of distilled water, and subsequently screened using a muslin cloth. The filtrate obtained was centrifuged at 4,500 rpm for 30 min (Type GLC-1 Ivan sorvall, Inc, USA). Starch obtained after centrifugation was reslurried in distilled water (5 L), and protein was separated from the starch by toluene emulsification. Toluene (50mL) was added to the starch suspension, and was thoroughly mixed for 30 min and then, the mixture was allowed to stand for another 5 h. An emulsion layer of denatured protein formed at the toluene–water interface and was discarded. The process was repeated for the starch slurry until the emulsion layer became less visible. The starch slurry was then washed with acetone and air dried for 24 h at 28 ^{o}C.

Starch acetylation

The method of Sathe and Salunkhe [12] was used for starch acetylation. One hundred grams of starch were dispersed in 500 ml of distilled water; then, it was stirred magnetically for 20 min. The pH of the slurry obtained was adjusted to 8.0 using 1 M NaOH. Over a period of one hour, 10.2 g acetic anhydride was added, while maintaining a pH range of 8.0 – 8.5. The reaction proceeded for 5 min after the addition of acetic anhydride. The pH of the slurry was adjusted to 4.5 using 0.5 M HCl. It was filtered, washed four times with distilled water and air-dried at room temperature (28 ^{o}C) for 48 h.

Determination of the degree of acetylation

The content of acetyl groups (expressed as percentage in dry basis) and the degree of substitution of acetylation were determined according to Lawal and Adebowale [21]. Five grams of acetylated starch were placed in a 250 mL volumetric flask, and 50 mL distilled water was added and mixed properly using a magnetic stirrer. Five drops of phenolphthalein indicator were added and the suspension was immediately titrated with 0.1 N sodium hydroxide until a permanent pink end point was obtained. Twenty-Five milliliters of 0.45 N sodium hydroxide solution was added to the mixture, the flask was sealed tightly with a rubber stopper and shaken vigorously for 30 min. The saponified mixture containing excess alkali was then titrated with standard 0.2 N Hydrochloric acid until the phenolphthalein color disappeared. The native starch was treated in the same manner to obtain a blank value.

$$\text{Percent acetyl (dry basis)} = \frac{\text{(Blank titre - Sample titre) ml X Acid Molarity X 0.043 X100}}{\text{Sample weight in g (Dry basis)}}$$

$$\text{Degree of substitution (D:S)} = \frac{162A}{(4300 - 42A)}$$

In which A = percent acetyl (dry basis).

Total ash and acid insoluble ash determination

Ash content was estimated by the measurement of the residue left after combustion in a furnace at 450º C [30]. The ash obtained from the determination of the ash was boiled with 25ml of 2M hydrochloric acid solution for 5 minutes, the insoluble matter was filtered, washed with hot water and then ignited. The weight was determined and the percent acid insoluble ash was calculated [30].

Moisture content and pH determination

One gram of sample was introduced into a crucible and transferred to a hot oven maintained at 120º C for 4 h. Afterwards, the hot crucible was transferred to a desiccator to cool and re- weighed. This was repeated until constant weight was achieved.

The pH of 1 % w/v slurry of each of the starches was determined using a pH meter (Corning, model 10 England) [30].

Flow Properties

Angle of Repose

The static angle of repose (a) was measured according to the fixed funnel and free standing cone method [19]. A funnel was clamped with its tip 2 cm above a plain paper placed on a flat horizontal surface. The powder was carefully poured through the funnel until the apex of the cone thus formed just reached the tip of the funnel. The mean diameter of the base of the powder cone was determined and the tangent of the angle of repose calculated using the equation:

$\tan \theta = 2h / D$ (where θ is angle, h is height of cone and D stand for the diameter of cone)

.

Bulk and Tapped Densities

Two grams of the powder sample was placed in a 10 mL measuring cylinder and the volume ($V_{o)}$ occupied by the sample without tapping was noted. After 100 taps on the table, the occupied volume V_{100} was read. The bulk and tap densities were calculated as the ratio of weight to volume (V_o and $V_{100,}$ respectively).

Hausners and Compressibility Index (C %)

Hausners Index was calculated as the ratio of tap density to bulk density of the samples (3, 4)

The Compressibility Index was calculated using the equation:
Compressibility= 100 X (Tapped density- bulk density)/ Tapped density.

Amylose and amylopectin

The method of Onah and Bristol [30] was adopted for these tests. Two grams of the defatted starch was suspended in 50ml of water; then added with stirring to boiling water butanol: water mixture (1:9 v/v). Butyl- and amyl alcohol (1:1 v/v) was added to the suspension and allowed to cool. The precipitate was centrifuged and washed repeatedly with butanol saturated with water to recover amylose. Amylopectin was similarly precipitated with excess methanol from the first supernatant.

Foam capacity

The method reported by Ihegwuagu *et al*. [30] was adopted. Two grams quantity of the native acha starch (NAS) was homogenized in 100ml of distilled water using a vortex mixer (Vortex-2 Genie set at shake 8) for 5 min. The homogenate was poured into a 250 mL measuring cylinder and the volume was recorded after 30seconds. The foam capacity was expressed as the percent increase in volume. Mean of three replicate tests is reported.

Emulsion capacity

A 2 g quantity of the NAS was dispersed in 25 mL of distilled water using a vortex mixer for 30 seconds. After complete dispersion, 25 mL of vegetable oil (ground nut oil), was added gradually and the mixing continued for another 30 seconds. The suspension was centrifuged at 1600 rpm for 5 min. The volume of oil separated from the sample was read directly from the tube. Emulsion capacity is the amount of oil emulsified and held per gram of sample [30].

Gelatinization temperature

The determination of gelatinization temperature was carried out using the differential scanning calorimetry.

Determination of water absorption capacity (WAC)

This was determined in accordance with the method described by Daramola and Osanyilusi [24]. 0.1 g of sample was weighed into a test tube. 10 mL of distilled water was added and heated in a water bath at 60º C for 30 min, centrifuged at 1000 rpm for

15 min and the supernatant was carefully decanted and the weight of the starch paste taken.

WAC = Weight of starch paste/ Weight of dry starch sample

Determination of solubility Index

1 g of starch in 20 mL of distilled water in a test tube was subjected to heating in water bath at 60º C for 30 min, centrifugation at 1200 rpm for 20 min and 10 mL of the supernatant was dried to constant weight. Solubility was expressed as percent by weight of dissolved starch [30].

Scanning electron microscopy (SEM)

Starch granule morphology was obtained using a Hitachi S5200 field emission scanning electron microscope (Hitachi High-Technologies Canada, Inc., Ontario, Canada). Images of platinum-coated samples were obtained at 1.0 kV accelerating voltage.

X-ray powder diffraction

Structural characterization was carried out using a Siemens D5000 X-ray diffractometer (Siemens, Munich, Germany). Powder samples, packed in rectangular aluminum cells, were illuminated using CuKα radiation (l = 1.54056 Å) at 45 kV and 40 mA. Samples were scanned between diffraction angles of 5 to 80^{o}. Scan steps of 0.1 were used and the dwell time was 15 s. A nickel filter was used to reduce the size (Kb) contribution to the X-ray signal. Triplicate measurements were made at ambient temperature. The degree of crystallinity was estimated utilizing the technique described by Nara and Komiya [20].

Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermograms were obtained using a DSC (Model DSC 204 F1Netzsch, Germany). The temperature axis and cell constant of the DSC cell were calibrated with indium (10 mg, 99.999 % pure, melting point 156.60 ^{o}C, heat of fusion 28.40 J/g). Starch samples (4.0 mg, dry weight basis) were weighed in aluminum pans on an analytical balance (Mettler Toledo AX-204, US). Approximately 9 µL distilled water was added to each sample pan and the pans were hermetically sealed. To account for the enthalphic contribution of water, the reference pans also contained 9 µL of distilled water. The samples were allowed to equilibrate for a minimum of 2 h and scanned from 26 ^{o}C to 180 ^{o}C at a heating rate of 10 ^{o}C /min under continuous nitrogen flow. Gelatinization parameters were characterized by onset temperature (*T*o; ^{o}C), peak temperature (*T*p; ^{o}C), conclusion temperature (*T*c; ^{o}C), and gelatinization enthalpy (D*H*gel; J/g). All parameters were calculated using the Universal Analysis software (TA Instruments, New Castle, DE). The gelatinization range (*R*gel; ^{o}C) was computed as (*T*c – *T*o) and the Peak Height Index (PHI; J g^{-1} K^{-1}) was calculated as the ratio of (D*H*gel/ *T*p – *T*o) [20]. Peak Height Index (PHI; J g^{-1} K^{-1}) is a ratio that helps compare quantitatively the variation in endotherm shape between samples. This ratio varies directly with enthalpy (D*H*) and inversely with the difference (*T*p – *T*o), and thus provides a numerical value that is

descriptive of the relative shape of the endotherm [20]. Statistical analysis was carried out on a sample size of $n = 5$.

Fourier transform infrared spectroscopy (FT-IR)
The IR spectra of starches were run as KBr pellets on impact 410 Nicolet FTIR spectrometer inthe frequency range 4000 –500 cm^{-1}.

Thermogravimetric Analyses (TGA)
Thermogravimetric analysis (TGA) was performed in a Thermogravimetric apparatus (Shimadzu, Japan). Sample (1.78 mg) was heated at a rate of 10 ^{o}C/min from ambienttemperature to 800 ^{o}C. Liquid nitrogen was used as the purge gas at a flow rate of 20 mL/min.

Statistical analysis
Statistical analysis was carried out using analysis of variance (ANOVA) using GraphPad Prism® (GraphPad Software Inc. San Diego, USA). Tukey-Kramer's multiple comparison tests was used to compare the physicochemical parameters of the starches. At 95 % confidence interval, P-values less than or equal to 0.05 were considered significant.

RESULTS

Organoleptic properties of the starches were similar: off white, gritty, non sticky with bland tastes. All the physicochemical indices (Table 1) investigated such as true density, bulk and tapped densities, water absorption capacity, moisture content, total and acid insoluble ash, pH and amylose content reduced after acetylation of acha starch. The foam capacity of AAS (2.00 %) is lower than that of NAS (5.30 %), while the emulsion capacity of AAS (45.00 %) was higher than that of NAS (31.90 %).

No obvious differences were observed in the morphology of the native and acetylated starch (Fig. 1). No pronounced difference was observed between the X-ray pattern of the native and acetylated starches (Fig. 2). The DSC thermograms for NAS and AAS are shown in Fig. 3 'A' and 'B' respectively and the corresponding parameters are tabulated in Tab. 2. Both starches showed two endothermic peaks and one exothermic peak. The peaks however, became slightly sharper after acetylation. The infrared spectra of the NAS and AAS are shown in Fig. 4 'A' and 'B', respectively. The results of Thermo gravimetric analysis for NAS and AAS are presented in Fig. 5 "A" and "B" respectively. Result of the swelling studies show that there was a significant ($P < 0.05$) increase in swelling index after acetylation implying that the modification resulted in weakening of associative forces in the starch molecules. All the samples gave the characteristic A pattern with strong peaks at about 15, 17, 18, 19 and 23^{o} θ. Similar observations have been reported in the literature. For example, Kuakpetoon and Wang [10] reported that there was no difference in the X-ray patterns for native corn starch and its chemically modified derivatives.

The degrees of crystallinity were 49.3 and 53.3 % for NAS and AAS respectively, suggesting that, acetylation did not have any significant effect on the crystallinity of

acha starch. This observation corroborates the SEM results which revealed that acetylation did not alter the granule morphology of acha starch. Both starches showed two endothermic peaks and one exothermic peak. The peaks however, became slightly sharper after acetylation, The To, Tp and Tc were respectively 90.6, 93.5 and 95.3 ^{o}C for NAS, and 87.3, 88.1 and 90.1 ^{o}C for AAS. The gelatinization enthalpies (δH) were 29.48 and 18.72 J/g for NAS and AAS, respectively.

DISCUSSION

Both NAS and AAS were dried under the same condition, therefore, the reduction in moisture content may be as a result of the substitution of the hydroxyl groups on the starch molecules as found also in other previous reports [21]. The reduction observed with the total and acid insoluble ash after acetylation may be attributed to the washing away of the mineral contents of the starches during acetylation. Lawal and Adebowale [21] had reported that, ash content of modified jack bean starch reduced considerably after modification and they attributed this observation to washing away of the starches mineral contents. The reduction in pH of acha starch after acetylation can be attributed to the introduction of acetyl groups on the starch molecules thereby increasing the acidity of starch molecules. The increase in swelling introduced after acetylation is very important especially in the application of this starch either as a drug carrier or disintegrant in tablets and capsule formulations.

Foam and Emulsion capacities

The foam capacitiy of AAS was lower than that of NAS, while the emulsion capacity of AAS was higher than that of NAS suggesting that the acetylated starch could find application as an emulsifier in the food industries [30].

Scanning electron microscopy

The biological origin of starch serves as a determining factor in the granule shape, size and morphology. As a result, these characteristics not only help to differentiate between various starches but also give an indication of the processing parameters. Different types of starches have been reported to have different morphologies ranging from oval, spherical, polygonal to irregular shapes [10, 19 – 21]. Fig. 1 shows the SEM for NAS and AAS respectively. In our investigation, no obvious differences were observed in the morphology of the native and acetylated starch. Although a similar observation by Lawal and Adebowale [21] was attributed to physiology of the starch granules and the level of modifications, it is reasonable to think that, acetylation of acha starch may not have destroyed the shape, appearance and structural arrangement of the starch.

"A" "B"

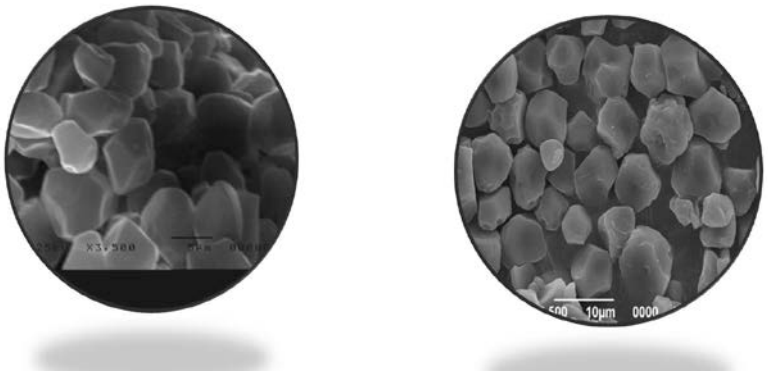

Figure 1: SEM of native (A) and acetylated (B) acha starches

X-ray diffractometry

Granular starches are usually found to give diffraction patterns that have been classified as A, B or C depending upon the arrangement of the double helical amylopectin chains [20]. The A-pattern is obtained as a result of a close packed arrangement with a water molecule between each double helix, while a more open hexagonal packing, with water molecules in the central cavity, exhibits a B-pattern [20]. Interplanar spacing and relative intensities of characteristic lines by which the three patterns can be differentiated are well documented in the literature [9, 10]. Usually the diffraction pattern is dependent upon the biological origin, but is also affected by other factors like amylopectin chain length, amylose and moisture content [9].

"A" "B"

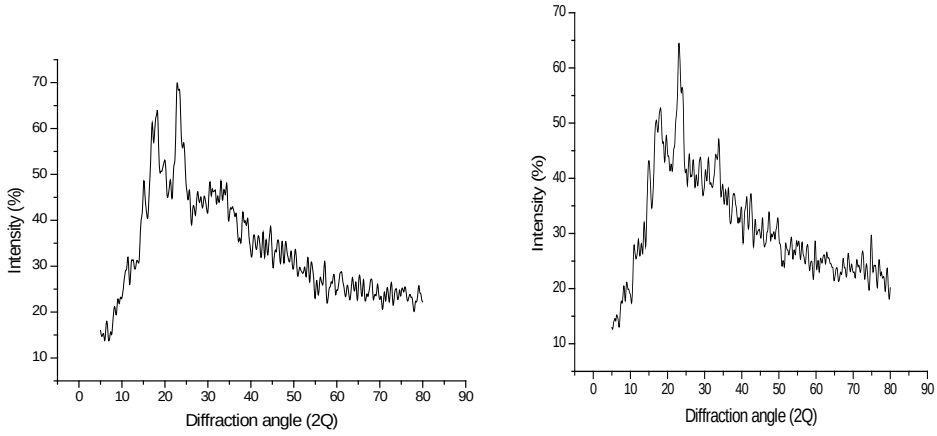

Figure 2: X-ray diffractogram of native (A) and acetylated (B) acha starches.

Differential scanning calorimetry (DSC)

Starch gelatinization is commonly described as a series of thermally associated events that convert an aqueous dispersion of starch into paste. From a thermodynamic standpoint, gelatinization refers to the enthalpic transitions involving the starch granule treated as a semi-crystalline entity (spherulite). Previous studies [20] proposed a comprehensive thermodynamic explanation of gelatinization based on the theory of polymer spherulites.

Because of its sensitivity and accuracy, differential scanning calorimetry has been extensively used to study the phase transitions of this process [20, 22]. The thermograms for NAS and AAS are shown in Fig. 3 "A" and "B" respectively and the corresponding parameters are tabulated in Table 2. The results in Fig 3 suggest some increase in crystallinity. The continuous endothermic transition noticed in both samples is indicative of granule swelling and crystallite melting occurring over the gelatinization range [20]. The gelatinization values above are consistent with those reported for other cereal starches [21]. The onset, peak, and conclusion temperatures of gelatinization of AAS were observed to be lower than that of NAS. Although the results obtained from the X-ray diffraction studies indicated that the degree of crystallinity of NAS was slightly lower than that of AAS (Fig 2), the DSC (Tab 2) results showed that, the enthalpy of gelatinization for NAS was considerably higher than that of AAS. Thus it was concluded that even though acetylation may have increased the crystalline regions, thereby conferring thermal and structural stability, the modification conferred faster gelatinization on the starch. The results from XRD and TGA studies substantiated the fact that the associative forces, which stabilize the granule structure in NAS were weak and were reinforced after acetylation. However, in the presence of moisture (as noticed during the DSC studies), the modified starch lost its stability. This observation corroborates our earlier results on the water absorption capacity (Table 1), and this new property is desirable in the pharmaceutical industry, where it can be employed as a disintegrant.

"A" "B"

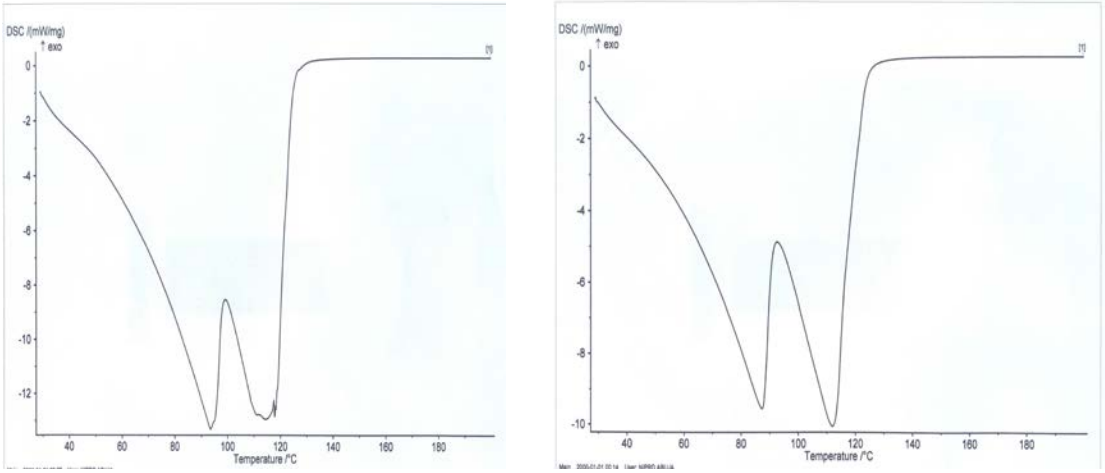

Figure 3: DSC thermogram of native (A) and acetylated (B) acha starches

Infrared spectrometry

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The infrared spectra of the NAS and AAS are shown in Fig. 4 "A" and "B" respectively. The band stretch around 3420 - 3538 cm^{-1} is attributed to hydrogen-bonded hydroxyls on the starch molecules. The band at 2929 - 2931 cm^{-1} is attributed to CH2 symmetrical stretching vibrations. In the native acha starch, the band at 1648 cm^{-1} is assigned to scissoring of two O–H bonds of absorbed water molecules. The bands at 856 and 764 cm^{-1} are due to skeletal stretching vibrations of starch. In the acetylated starch, the weak peak at 2379 cm-1 describes the -NH- in the starch molecule, the sharp band displayed at about 1648 cm-1 may be due to the stretching vibration of carbonyl group. The new band introduced at 1728 cm-1 confirms that acetylation took place on the starch molecules [10].

"A" "B"

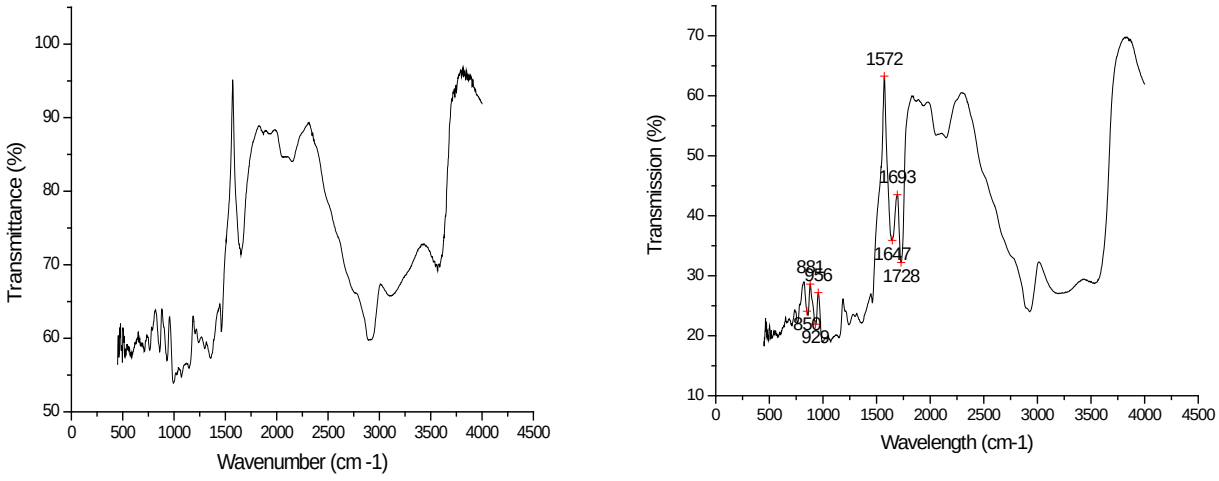

Figure 4: FTIR spectrum of native (A) and acetylated (B) acha starches

Thermal stability

Thermo-physical parameters provide vital information about the thermal stability of polymeric materials. In our case, three step thermograms were noticed in both the native and acetylated starches (Fig 5). AAS showed progressive decompositions to be 12.31, 57.69 and 27.69 % successively. The studies indicate that the maximum degradation occurred within the range 128.57–342.86 ^{o}C. Successive decompositions for NAS were 11.43, 58.57 and 28.57 %. In addition, the range of maximum decomposition was within 127.27–327.27 ^{o}C. The early minor weight loss (TG) in both samples can be attributed to desorption of moisture as hydrogen bonded water to the polysaccharide structure. Although the result showed that there was a slight increase in the thermal stability of the modified starch, the difference in the decomposition pattern of the two starches was not significant as about 58 % of the acetylated starch decomposed within the similar range where 59 % of the native starch decomposed. The reason for the higher IDT of AAS is the heterogeneity that results after modification (21). Although increase in thermal stability after acetylation has been reported for other polysaccharides such as hemicelluloses [29], the result obtained showed that, the degree of acetylation of starch may be responsible for the

extent of thermal stability conferred. The main decomposition mechanism of starch is the dehydration reaction between starch hydroxyls; this suggests that the smaller the amount of hydroxyl group left on the starch, the more stable it becomes. This position was corroborated in the higher thermal stability of methylcellulose compared with the unmodified cellulose [29].

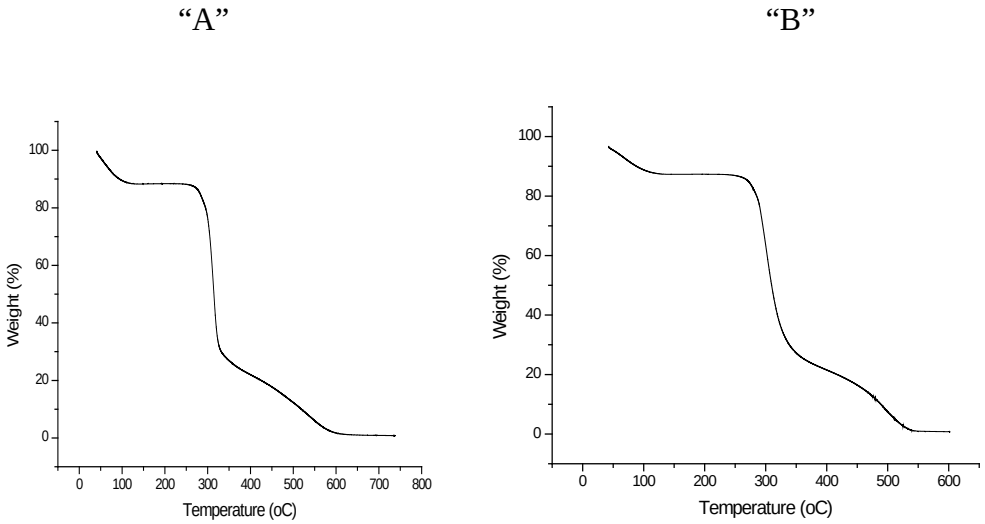

Figure 5: TG thermogram of native (A) and acetylated (B) acha starches

CONCLUSION

This study provides the first comprehensive report on the physicochemical properties of starch isolated from the grains of *Digitalis exilis* and predicted its suitability as an excipient in both the pharmaceutical and cosmetic industries. The ease of modification coupled with improved properties conferred on the modified product, shows that, this starch holds great promise for commercial exploitation. Thermal stability increased after modification and a tendency for increased water absorption was also observed. For technical applications, such as the preparation of super-absorbent hydrogels, preparation of biopolymer based flocculants, drug-release and other applications where bio-based polymers are relevant, acetyl acha starch could be strategic because the source material is reasonably cheaper than other conventional sources of starch and does not compete with man as major source of staple food. This report should provide relevant information to biopolymer-based industries.

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Table 1: Some physicochemical properties of native and acetylated starches

S/N	*Parameters*	*Native Acha Starch*	*Acetylated Acha Starch*
1	Total ash (%)	0.50 ± 0.01	0.20 ± 0.01
2	Water-soluble ash (%)	0.00 ± 0.00	0.00 ± 0.00
3	Acid insoluble ash (%)	0.02 ± 0.01	0.00 ± 0.00
4	True density (g/ml)	1.57 ± 0.01	1.44 ± 0.02
5	Amylose: amylopectin ratio (%)	20:80 ± 0.04	19:81 ± 0.02
6	Angle of repose (o)	ND	36.43 ± 2.30
7	Degree of substitution	NA	0.76 ± 0.02
8	pH	6.90 ± 0.04	6.40 ± 0.01
9	Bulk density (g/ml)	0.56 ± 0.01	0.41 ± 0.03
10	Tapped density (g/ml)	0.76 ± 0.01	0.64 ± 0.01
11	Moisture content (%)	11.00 ± 0.04	10.00 ± 0.03
12	Gelatinization temperature (^{o}C)	93.5 ± 0.00	87.3 ± 0.00
13	Foam capacity (%)	5.30 ± 0.00	2.00 ± 0.00
14	Emulsion capacity (%)	31.90 ± 0.08	45.00 ± 0.50
15	Water absorption capacity (%)	110.00 ± 2.01	430.80 ± 5.01

ND; could not be determined, NA; not applicable.

Table 2: Thermal properties of NAS and AAS Starches

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Parameter	NAS	AAS
Onset temperature (T_0)(^{0}C)	90.6	87.3
Peak temperature (Tp) (^{0}C)	93.5	88.1
Conclusion temperature (Tc)(^{0}C)	95.3	90.1
Enthalpy of Gelatinization [J/(g*K)]	29.5	18.7
ΔT (Tc- T_0)	4.7	2.0
Peak Height Index (PHI)	0.62	0.29

NAS; native acha starch, AAS; acetylated acha starch

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