Assessment of Nutritional and Physicochemical Characteristics of Unmodified and Chemically Modified Water Yam *(Dioscorea alata)* Starches

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Abstract

Starch is a polymeric carbohydrate which is made up of several glucose units connected by glycosidic linkages. It can be sourced from plant tubers and grains. With the increase of new food and non-food industries, more starch is needed as a raw material and there is the need to look for alternative sources of commercial starch. In this study, starch was extracted from water yams (*Dioscorea alata*), which is considered as lesser yam and thereafter, modified chemically via acetylation, oxidation, and a combination of acetylation and oxidation processes. Using established techniques, the physicochemical characteristics and nutritional makeup of the unmodified and chemically modified water yam starches were assessed, and the outcomes were compared. Assessment using a Fourier Transform Infrared spectrophotometer (FTIR) was carried out to ascertain how the functional properties of both unmodified and modified starch had changed. The moisture content of modified starches was higher, while the ash, fat, and protein contents were lower in comparison with the unmodified. Compared to other starch samples, acetylated/oxidized starch exhibited a higher swelling power, a better ability to absorb water and oil, and a higher content of crude fiber. Compared to unmodified starch, oxidized starch was more soluble. When comparing unmodified starch to modified starch, FTIR analysis showed differences in the absorption bands of the former at 3389 cm^{-1} (O-H), 2932 cm^{-1} (C-H), and primary, secondary, and tertiary amide moiety at 1079, 1643, and 1205 cm^{-1}, respectively. The physicochemical and nutritional properties of the starch were generally affected by modification making them a potential excellent material for industrial applications.

Introduction

Starch is the most abundant carbohydrate storage found in plants and cyanobacteria [1]. It is a polymeric form of carbohydrate which comprises of vast array of glucose unit joined by a glycosidic bond. In its pure form, starch is a white, tasteless and odorless powder soluble in cold water and alcohol and is comprised of amylose and amylopectin. It is produced in the chloroplasts of green leaves during photosynthesis and are stored in the amyloplasts in cereals and tubers [2, 3]. Starch can be obtained from cereal grains such as rice, millet, corn, wheat and root tubers like yams, cassava, potato etc. Although there are some unutilized grains and tubers that need to be considered for commercial starch production, in which water yam is one of such. Starch is a raw material of immense value due to its countless application in the industries, agriculture and homes [4]. In its unmodified form, starch has some limitations which include low shear stress resistance, thermal decomposition at high temperature, high retro-gradation and syneresis thereby limiting its industrial applications, especially in food and pharmaceutical processes. These therefore necessitated its modification in order to enhance its versatility, improve its applications and satisfy consumer demand [5]. Starch research is interesting because of how easily its structure can be changed and this will have effects on its functional properties like size, shape and chemical composition. Modifying starch improves the functionality by amending its physical and chemical properties or by adding new features [6, 7]. Modification of starch changes the structure of starch, as a result of which its properties change and allows expansion in its practical application [8]. It has been shown that starch can be blended with natural rubber [9] and inert synthetic rubber/recycled-used polymer to obtain an environmentally friendly product that is cheap and biodegradable [10]. In pharmaceutical industries, starch is used as excipients such as binder, lubricant, glidants, and fillers. Yam (*Dioscorea* spp.) is a nutritional and medicinal staple tuber crop grown in subtropics and tropics. Among the yam species is water yam (*Dioscorea alata)*. It originates from south East Asia and is widely spread throughout the world. The tuber shape is generally cylindrical in shape but can come in various shapes. Its flesh is white but sometimes purple and watery which ascertains it name as 'Water yam'. *Dioscorea alata* can be stored for a longer period of time (5–6 months) than other yam species and has the higher yielding capacity among them, it is also known as the greater yam. With a crude protein content of 7.4%, a starch content ranging from 75–84%, and vitamin C content ranging from 13.0 to 24.7 mg/100 g, water yams are also well-known for their high nutritional content [11, 12].. *Dioscorea alata* being less common than the *Dioscorea rotundata* variety are valued for their bulk, high moisture content, and starch content [13]. With the upcoming food and cosmetic industries, there is the need for more commercial starch. The aim of this work is to chemically modify the unmodified starch obtained from *Dioscorea alata*, ascertain its properties and enhance its performance in different compositions for food and non-food industries which will reduce pressure on established sources of commercial starch by increasing D. alata's commercial use and, eventually, strengthening the economy.

Methodology

Source

Water yam (*D. alata)* tubers were purchased at Bodija market, Ibadan. They were washed, cleaned and identified at Botany department, University of Ibadan.

Extraction of starch from water yam

The starch was extracted using the wet method as described by Benesi [14], with slight modification. Water yam was peeled and cut into smaller pieces and homogenized with excess distilled water in a blender. The slurry was filtered through a muslin cloth followed by a sieve of 200 mm mesh to remove impurities followed by sedimentation. The supernatant was discarded and the sediment (starch) was washed several times with distilled water. The starch was oven dried at a temperature of 40 ^{o} C for 12 hours. The dried starch granule was stored for use.

Chemical modification of starch

Three chemical modifications were carried out on the unmodified starch which included: Acetylation, Oxidation and Acetylation/Oxidation

Preparation of acetylated starch, oxidized starch and acetylated/oxidized starch

These modifications were carried out using Sathe and Salunkhe's [15] method.

Nutritional content of unmodified and modified starch

Proximate Analysis

The nutritional compositions of the powdered sample were determined by using the method of AOAC [16].

Physicochemical and Functional Properties of Starch

- Viscosity Measurement

Viscosity was measured using Ostwald viscometer. This viscometer was calibrated with water and 20% aqueous solution of sucrose. The liquid was drawn into the upper bulb until the meniscus was few centimeters above the highest mark. The stop watch was started as the meniscus passed through the higher mark. The stopwatch was stopped as the meniscus passed the lower mark with reproducibility of a few tenth of a second. 2g of starch was dissolved in 100 mL of water and measured using a viscometer.

- Swelling Power and Starch Solubility

About 1.0 g of starch sample was weighed and transferred into a clean & dried test tube and re-weighed with the test tube (W_1). The starch was then dispersed in 50 cm^3 of distilled water using a blender. The resultant slurry was heated at temperature; 55, 65, 75, 85, 95 ^{o} C for 30 min in a water bath. The mixture was cooled to 30 ± 2 ^{o} C and centrifuged (500 rpm, 15min). An aliquot (5 mL) of the supernatant were dried to a constant weight at 110 ^{o} C. The residue obtained after drying the supernatant was recorded as the starch solubilized in water. Solubility was calculated as g per 100 g of the 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).

Swelling test (%) = [W_2 – W_1] / weight of starch x 100.

- Water and oil Absorption Capacity

Water absorption capacity was determined using the centrifugal method. 1.0 g of the sample was mixed with 10 ml distilled water or oil in a 50 mL centrifuge tube. The content was stirred for 3 minutes. The content was centrifuged for 30 minutes at 5000 rpm. After which the content was allowed to stabilize and the supernatant was carefully decanted into a graduated measuring cylinder

% Water or oil Absorption Capacity = $\frac{Weight\ of\ water\ absorbed}{Weight\ of\ sample}$ x 100

- Fourier transform infrared spectroscopy of starches

FTIR analysis was carried out using FTR-(Bruker-Alpha, Platinum ATR) machine which uses the Automated Total Reflectance (ATR) technique.

Results and discussion

Proximate composition

The chemical composition of the acetylated starch (Ace), oxidized starch (Oxi), Acetylated/oxidized starch (Ace/Oxi) and unmodified starch (NatS) of water yam are shown in Table I below.

Table I: Proximate Composition of Unmodified and modified starches

Sample	Moisture content (%)	Ash content (%)	fat content (%)	Crude fibre (%)	Crude protein %	Carbohydrate content (%)
Ace	18.00 ± 0.16	5.33 ± 0.52	0.24 ± 0.03	1.79 ± 0.20	1.09 ± 0.12	75.34 ± 0.03
Oxi	18.66 ± 0.16	4.00 ± 0.15	0.23 ± 0.04	1.96 ± 0.30	1.03 ± 0.18	76.08 ± 0.70
Ace/Ox	19.33 ± 0.9	3.30 ± 0.17	0.28 ± 0.06	2.00 ± 0.20	1.14 ± 0.07	75.95 ± 0.57
NatS	17.33 ± 0.8	6.60 ± 0.79	0.35 ± 0.07	2.04 ± 0.19	1.58 ± 0.37	74.14 ± 0.23

Mean ± SD. Mean with different superscript letters along a column are significantly different ($p < 0.05$).

Ace: Acetylated starch, OxI: Oxidized starch, Ace/oxi: Acetylated/oxidized starch NatS: Unmodified Starch

Acetylated oxidized starch is a chemically modified starch in which dual treatment of both acetylation and oxidation is carried out on the unmodified starch and in this process the starch is treated by sodium hypochlorite then esterification with acetic anhydride is carried out according to GMP [17]. These chemical modifications had effects on the nutritional and physical characteristics of the starch which is an additional advantage in both food and cosmetic industries. The nutritional characteristics of acetylated, oxidized, acetylated/oxidized and unmodified starch of water yam were used in the study and the results are shown in table I above. It showed the percentage variation of moisture, ash, fat, crude fibre, crude protein and carbohydrate, the moisture content was seen to be higher in the chemically modified starches than in the unmodified starch with the value of 19.33 ± 0.9% for acetylated/oxidized starch and 17.33 ± 0.8% for unmodified starch. This indicated that chemical modification could increase the moisture content of the starch. Similar observation has been reported in the earlier research work that acetylation increased the moisture content of starch by weakening the bonds that exist in the starch molecule thereby making the granules of the starch to swell or be more soluble in solvents [18].The value of ash content was seen to have reduced from 6.60 ± 0.79% for unmodified starch to 3.30 ± 0.17% for acetylated/oxidized starch. Similar observation has been reported in the earlier research that acetylation method reduces the ash content of starch. This modification reduced the ash content of food which is an indication to the level of availability of minerals. The ash content of starch is typically less than 0.5% of the dry matter [18]. However, the considerably high values of ash content obtained for the unmodified starch studied may suggest the high level of availability of minerals in the water yam starch. The fat content was also reduced by the chemical modification of the unmodified starch of water yam. According to Rincón[19] acetylated and oxidized starches were seen to have lower amounts of ash, crude fibre and protein when compared with their unmodified starch and the same trend was seen in this study as the chemically modified starches showed a similar trend of reduction in ash, crude proteins, fats and crude fibre when compared to the unmodified starch of water yam. Fat content signifies the presence of essential fatty acid; it was shown in this study that the unmodified starch had higher fat content than the chemically modified starches. Crude protein is related to oil absorption, as the nonpolar protein chain sites have the ability to absorb oil [6].

Table II: Results of Physicochemical properties of Unmodified and Modified Starch of Water Yam

Sample	Swelling power (%)	Solubility (%)	Water absorption capacity(%)	Oil absorption capacity(%)	Viscosity (centipoise)	pH
Ace	9.98 ± 0.02	8.21 ± 0.91	90.81 ± 0.12	73.78 ± 0.37	0.833 ± 2.69	4.58
Oxi	9.65 ± 0.30	11.01 ± 0.80	90.52 ± 0.17	74.50 ± 0.01	0.912 ± 2.61	8.20
Ace/oxi	10.92 ± 0.90	10.10 ± 0.89	92.08 ± 0.13	76.90 ± 0.47	0.861 ± 2.66	9.72
Nat/S	9.48 ± 0.5	7.52 ± 0.16	89.35 ± 0.14	72.90 ± 0.81	0.917 ± 2.60	6.49

Mean ± SD.

Ace: Acetylated starch, OxI: Oxidized starch, Ace/oxi: Acetylated/oxidized starch NatS: Unmodified Starch

Acetylated starch (Ace) as shown in table II has higher swelling power than the unmodified starch, although the acetylated-oxidized starch had the highest swelling power. Acetylation treatment had been noted to increase the swelling and solubility of the grain that has been acetylated. The effect of acetylation on grains has been reported by Cisse [20] and Sodhi [21]. The increases in swelling power of the grain after acetylation can be deduced by the presence of hydrophilic acetyl groups which allows water molecules to be retained due to the formation of hydrogen bonds [20]. The retention of the water penetrates the granules of the grain and thus increases the swelling and promotes gelatinization. The ease at which the acetylated grains absorb water is reflected in its solubility and water absorption capacity, the increase in water absorption capacity after acetylation treatment of the grain has been reported by Cisse [20] and Lawal [22] to be higher than its unmodified starch. The introduction of acetyl group and oxygen caused electrostatic repulsion among starch molecules, which allowed water and oil to be readily absorbed into the modified starch matrices thereby improving the water absorption capacity and oil absorption capacity [23]. The increase in water absorption capacity has always been associated with increase in the amylose leaching and solubility, and loss of starch crystalline structure. The starch with high water absorption may have more hydrophilic constituents such as polysaccharides. The ability of starch to absorb water is an indication of its moisture stability that is very important for food industry [6]. The acetylated starch showed the ability to absorb oil more than the unmodified starch. Due to the oil absorption ability of acetylated starch, it could be used in the food, pharmaceutical and cosmetic industries; The introduction of acetyl groups reduces the resistance of bonds between the starch molecules. Acetylated starch increases the swelling capacity and solubility compared to native starch. Modification generally influenced the physicochemical and nutritional properties of the starch. Thereby placing them as a good material for industrial uses [24].

The FTIR results of both the unmodified and modified samples of water yam starches were shown in Fig I. The FTIR analysis was carried out in order to determine the effects of modification on the starch matrices. The diagnostic absorption band of O-H moiety can be found around 3600–3300 cm^{-1} which is as a result of energy absorption transmittance of hydroxyl group [25]. A broad O-H peak at 3389 cm^{-1} was observed in the unmodified starch spectrum Fig, 1(a). However, variation in which a shift to lower absorption frequency were observed in the modified sample at 3382, 3269 and 3362 cm^{-1} for Oxl, Ace and Ace/Oxl samples respectively. The absorption bands within the range of 2800–3000 cm^{-1} wavelength is a characteristic absorption band of sp^2 and Sp^3 hybridized CH bonds stretching. Intensity of bands in this region is as a result of the presence of amylose and amylopectin contents of starch. The unmodified CH absorption band was observed at 2932 cm^{-1} as shown in Fig I(a). Mild variation was observed in the absorption bands of the modified samples at a varying absorption value of 2927,2922 and 2930 cm^{-1} Oxl, Ace and Ace/Oxl samples respectively. Therefore, the observed variation in the intensities of CH transmittance bands within this region by the modified samples was due to differences in amylose/ amylopectin contents of the starches [5, 26]. It has been earlier reported by Kizil [26] that the increase in the intensity of absorption corresponds to a decrease in the amylose content of a starch. The result of this study however showed that the amylose contents of the modified samples were observed to be increased due to modifications, with Ace/Oxl sample having the highest amylose content at 2922 cm^{-1}, followed by Oxl at 2927 cm^{-1} and Ace/Oxl at 2930 cm^{-1} compared to the NatS at 2932 cm^{-1} [5].

Characteristic absorption band of primary and secondary amide were found in 1079 and 1643 cm^{-1} respectively for NatS sample. The tertiary amide absorption of NatS bands was observed at 1204 cm^{-1}. This is as a result of the stretching vibration of C-N bond and slight shift or perturbation of N-H bonds which are bands located within the protein groups thereby indicated the presence of residual proteins within the starch matrices [27]. A variation in the amide absorption band of the modified samples was observed as shown in Fig I(b–d). This phenomenon is due to the modification of the starch samples.

Furthermore, series of prominent absorption bands observed within the region 997–999 cm^{-1} shown Fig I(a-d) is due to the relative differences in the crystallinity of the starches [5, 28].

Conclusion

It showed that modification actually took place and had effect on the physical and nutritional properties of the natural starch. The modification took place in three steps which included: acetylation only, oxidation only, then a combination of acetylation and oxidation which gave different results in their physiochemical properties, nutritional properties and adsorption bands in the infra-red region. Oxidized starches have have high clarity or transmittance, low viscosity, and low temperature stability, it could be used in confectioneries for coating candles and sweets which easily melts. Therefore, chemically modified starch of water yam could be used in the food and non-food industries. However, high value of crude fibre was shown by acetylated/oxidized (dual modified method) starch of water yam. Starch usage is encouraged because it is cheap, abundant, has a non-toxic nature and easily biodegradable. Acetylated oxidized starches could be used as thickener, stabilizer, binder and emulsifier in food and non- food industries.

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Figures

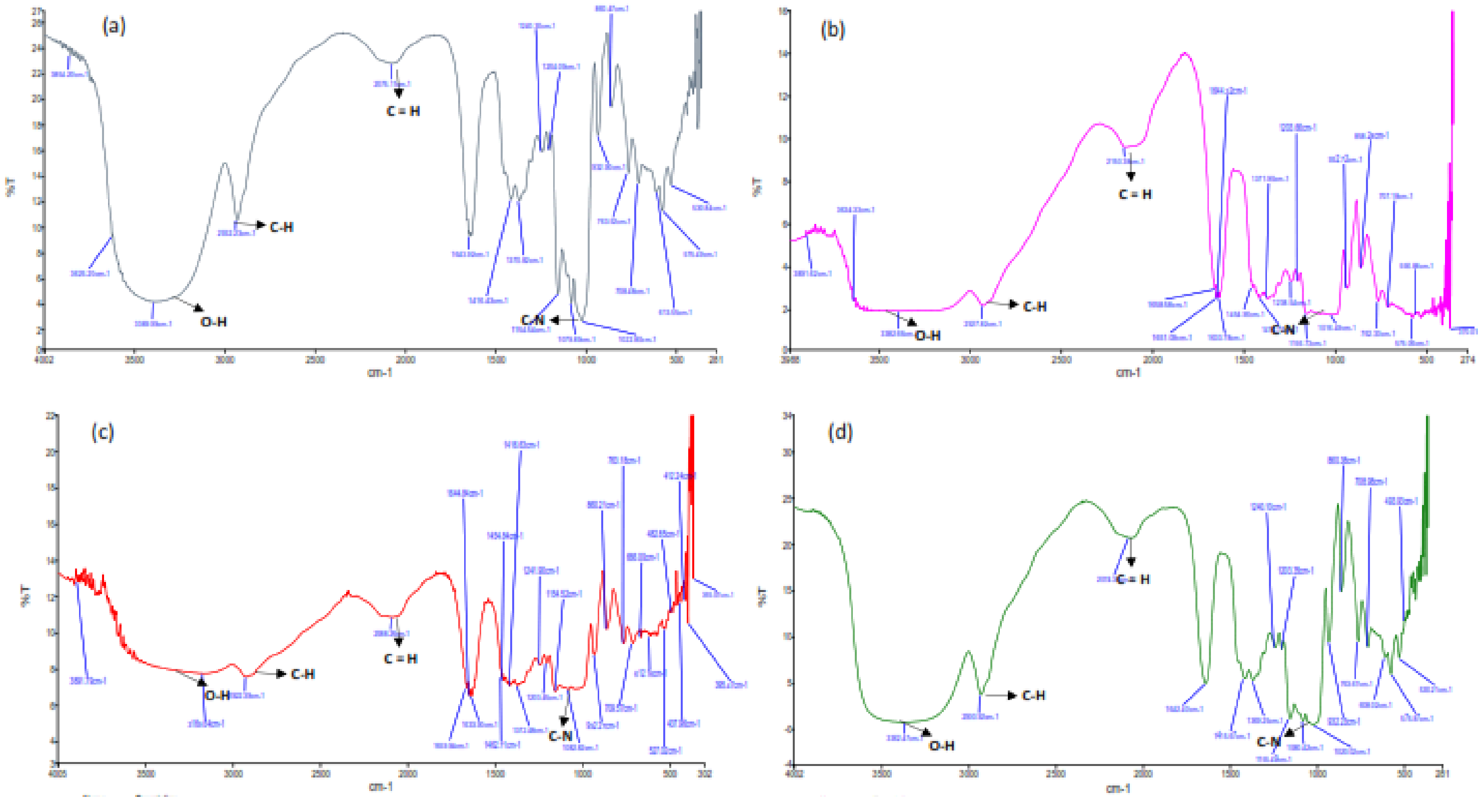

Figure 1

The FTIR of unmodified and modified starch of water yam (*Dioscorea alata*) (A: Unmodified starch, B; Oxidized starch, C; Acetylated starch, D: Oxl: Acetylated/oxidized starch)