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Structural and physicochemical properties of heat moisture treated and citric acid modified acha and iburu starches

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ABSTRACT

Starches extracted from *acha* (*Digitaria exilis*) and *iburu* (*Digitalia iburua*) were subjected to heat moisture treatment and citric acid modification. Successful applications of the treatments are expected to promote commercial utilization of the starches from these underutilized crops and improve the economy and livelihood of stakeholders along their value chains. Granules of the starches from the two cereal grains were polyhedral in shape. Generally, modifications led to the clustering of the polyhedral of the starches granules. Indentations were observed on the surfaces of citric acid modified (CAM) starches. This could be due to the weathering effect of acid hydrolysis. Modification methods employed did not affect the characteristic type-A crystal polymorph of the native starches. The starches generally exhibited single prominent peaks at (2θ) 16 and 24, and a doublet at 17-19. Crystallinity index of the starches ranged from 27.01-27.84% for *acha* and 29.01–30.47% for *iburu*. FTIR analysis and high peak gelatinization temperatures of the starches suggested heterogeneity in the matrices. CAM starches of the two grains remained in liquid form throughout the pasting cycle. *Acha* starches are lighter and whiter in color. All the starch samples exhibited promising functional properties that could place them as good materials for different industrial uses. Results of this study further exposed the potentials of *acha* and *iburu* starches for food and pharmaceutical applications.

1. Introduction

The continued interest in starch research stemmed from its array of functional properties. These properties place it as an indispensable ingredient for innumerable domestic and industrial applications (Alimi, Workneh, & Sibomana, 2016a). Utilization of starch in food system is dictated by its dominant properties. For instance; starch contribution to the textural properties of some foods makes it an important agent of thickening, stabilizing, gelling, bulking and water retention (Singh, Kaur, & McCarthy, 2007). Its lipophilic property is also important in fat based food. However, these properties vary according to the biological source of the starch and are governed by the size, shape, structure and chemical composition of its granules (Zavarese & Dias, 2011). Interestingly, starch in its natural form has some shortcomings which limit its use in industrial food processing. Examples of these shortcomings include its inability to withstand the high temperature, pressure and some strong chemical reagents use in most industrial food and pharmaceutical processes. Hence, starch is modified to correct some or all of these anomalies (Alimi, Workneh, & Oke, 2016b).

Properties of native and modified starches from major cereal and leguminous crops have been studied over time. The new thrust in starch research is the exposition of the potentials of starch from underutilized crops that have significant starch content. Some of these crops are abundantly available in developing countries. Successful isolation, characterization and further improvement of the starches from these crops would promote utilization of the starches and expand sources of starch. This would reduce pressure on established sources. It would also enhance commercial utilization of these crops and ultimately improve the economy and livelihood of farmers and other stakeholders along their value chains (Alimi et al., 2016a).

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Acha (*Digitaria exilis* Stapf) and *iburu* (*Digitalia iburua* Stapf) belong to this class of underutilized cereal crops. They are mostly grown in West Africa and were described as small seeds with big promises because of their excellent agro-ecological and food values. They perform excellently well on low moisture and fertility soil that may not support other cereal crops. They are known to mature within a short period of 6–8 weeks, have high starch content and higher economic returns compared to other cereals (Arueya & Oyewale, 2015; Jideani & Akingbala, 1993). Philip and Itodo (2006) reported that *acha* and *iburu* have greater performance potentials than some major cereal crops when same quantity of extra inputs are applied during growing period.

Acha and *iburu* grains have good content of sulphur amino acids. Sulphur amino acids are known for their importance in proper heart functioning and nerve transmission (Jideani & Jideani, 2011). They were also believed to have neutraceutical potential because of their use in some culture to manage diabetes (Jideani & Jideani, 2011).

However, the major attraction of these grains to researchers is their high starch content of about 75.5% (Arueya & Oyewale, 2015). Hence, studies are being carried out continuously to characterize their starches. These are with the view of exposing their potentials for domestic and industrial applications, and enhancing their values. Primary work on the properties of native *acha* and *iburu* starches was conducted by Jideani and Akingbala (1993). They were further investigated by Jideani, Takeda, and Hizukuri (1996). The studies revealed that the starches have properties typical of non-waxy cereal starches. However, native starches from these grains have characteristic shortcomings that are general to starches in their natural form. These shortcomings limit their industrial applications (Emeje et a. 2012). Hence, studies are being conducted to improve on the properties of their native starches (Emeje at al. 2012; Olu-Owolabi, Olayinka, Adegbemile, & Adebowale, 2014; Arueya & Oyewale, 2015). However, reports on heat moisture treatment and citric acid modification of the starches from these grains are scarce in literature.

There are different starch modification methods. The choice to be employed is dependent on the intending industrial end-use of starch. Heat moisture treatment, a type of hydrothermal modification, is a preferred method of starch modification for food and pharmaceutical applications. This is mainly because of the safety of heat moisture treated starch to health of consumers (Alimi, Workneh, & Oyeyinka, 2017). Heat moisture treatment also imparts favorable changes to the properties of starch. The enhanced properties are essential for some specific industrial applications (Alimi et al., 2016a). On the other hand, citric acid modification is a mild acid treatment of starch. It is relatively safe for food and pharmaceutical uses; since organic acid is the major treatment agent as compared to mineral acids. Citric acid modified starches find important applications in products where clarity is of essence. Examples include cheese and candies. Therefore, successful modification of the starches from *acha* and *iburu*, using these two modification methods, could expand their potential utilization for food and non-food uses. Hence, the objectives of this study were to investigate the effects of heat-moisture and citric acid modifications on some physicochemical properties of *acha* and *iburu* starches.

2. Materials and methods

Good quality *acha* and *iburu* were purchased from a local market in Kano, Nigeria. Native starch was extracted according to the alkaline (using aqueous sodium metabisulphite) steeping method previously reported by Arueya and Oyewale (2015). Toluene emulsification was used to separate protein from starch. Starch obtained was dried in a forced convective air oven at 45 °C for 24 h, packed in an airtight Ziplok bag and stored at 4 °C until further analyzes.

2.1. Heat-moisture treatment

Heat moisture treatment was carried out on native starches of *acha* and *iburu* as described by Alimi et al. (2016b). Moisture content of the starches was determined and raised to 25% through dispersion in distilled water. The slurries were heated in a convective hot air circulation oven at 110 °C for 16 h. The heat moisture treated starches obtained were left to cool, packed in Ziploc bags and stored at 4 °C until further analyzes.

2.2. Citric acid modification

Protocol described by Falade and Ayetigbo (2015) were used to prepare citric acid modified starches. Native starches (300 g) were dispersed in distilled water (400 mL) to obtain starch suspensions. The suspensions were brought to alkaline pH (about 9) through addition of 10 mL of 1 M NaOH and held for 30 min. The suspensions were intermittently stirred during the holding period. Citric acid (15% of weight of dry starch) and sulphuric acid (1% by weight of dry starch) were carefully added to distilled water to make 100 mL acidic solution which was then added to alkaline suspensions. The mixtures were left for 5 h at prevailing laboratory condition. The mixtures were then washed with 600 mL distilled water, filtered to remove excess liquid and dried in a convective hot air oven at 50 °C for 24 h. They were then milled, packed and stored as indicated above.

2.3. Scanning electron micrograph

Thin layer of starch samples was mounted on stubs with the aid of double-sided adhesive tape and sputter-coated with gold using EIKO IB-3 ion coater (EIKO Engineering, Hitachinaka, Japan). Morphology of starch granules was thereafter captured with a scanning electron microscope (EVO LS 15, ZEISS International, Oberkochen, Germany). Sizes of the granules were measured using an image analysis software (AnalySIS, Soft Imaging System, Berlin, Germany).

2.4. X-ray diffraction

An X-ray diffractometer (D8 Advance, BRUKER AXS, Germany) coupled with a sample changer and image plate detector was used to capture the diffraction patterns of the starches. The scanning was registered at Bragg angle (2Θ) 3° to 40° at scan step 0.035° and step time 0.5 s. Multi peak fittings to get integrated areas of crystalline peaks (*Ac*) and amorphous peaks (*Aa*) were done using EVA software (BRUKER, Germany). Crystallinity index (*Xc*) was calculated as below

$$Xc(\%) = \frac{100Ac}{(Ac + Aa)} \quad (1)$$

2.5. Infrared spectra

Infrared (IR) spectra of native and modified starches were obtained with the use of Fourier Transform Infrared (FTIR) spectrometer (Spectrum 100 series, Perkin Elmer, Beaconsfield, UK). The wavelength range was 4000 to 380 cm^{-1} at resolution of 4 cm^{-1}.

2.6. Thermal properties

Starch Thermal properties were evaluated using a TGA/DSC (Perkin-Elmer Inc. USA) coupled with data analysis software. Distilled water (6 μL) was added to starch in DSC (aluminium) pan. The pan was sealed, reweighed and left for 2 h for equilibration of starch and water. Scanning was done between 40 and 140 °C at stepwise increase of 10 °C/min and at 140 °C for 5 min (gelatinization). Empty pan was used as reference. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy (ΔH, J/g), for gelatinization were determined.

2.7. Pasting properties

The pasting properties of the starches were determined with a Rapid Visco Analyzer (RVA model 4500, Perten Instruments, Australia) using the protocol described by Alimi, Sibomana, Workneh, and Oke (2016c).

2.8. Color parameters of the starches

The Commission Internationale de l'Eclairage (CIE) L^*, a^* and b^* parameters were determined with the aid of a colorimeter (Chroma meter CR 400, Konica Minolta, Japan). Duplicate measurements of the color parameters were taken after standardizing the colorimeter using white tile. Hue angle (H), color intensity (ΔE) and the degree of whiteness (W) were calculated using the equations below.

$$H = \tan^{-1}(b^*/a^*) \quad (2)$$

$$\Delta E = \left(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\right)^{0.5} \quad (3)$$

$$W(\%) = 100 - \left[(100 - L^*)^2 + \left((a^*)^2 + (b^*)^2\right)\right]^{0.5} \quad (4)$$

2.9. Functional properties

Water and oil absorption capacities, swelling power, solubility and alkaline water retention of native and modified starches of *acha* and *iburu* were determined as described by (Alimi et al., 2016a). Emulsion capacity and relative occluded volume of the starches were determined as described by Falade and Ayetigbo (2015).

Least gelation concentration was determined as described by Alimi et al. (2016a). Starch sample was dispersed in separate test tubes each containing 5 mL distilled water in the ratio of 2–20% of distilled water at 2% increasing order. The dispersion was heated in water bath at 80 °C for 1 h, then rapidly cooled under running tap water and stored at 4 °C for 2 h. The lowest concentration at which the gel formed did not fall from the inverted tube was the least gelation concentration.

2.10. Data analysis

Experiments were carried out at least in duplicates and the data were analyzed using Analysis of variance tool in SPSS (15.0) environment. Means with significant differences at $p \leq 0.05$ were separated using Duncan Multiple Range Test (DMRT).

3. Results and discussion

3.1. Morphological properties

Structure of native and modified *acha* and *iburu* starches are presented in Fig. 1. Granules of the starches from the two cereal grains are polyhedral in shape as previously reported by (Jideani et al., 1996). Though none of the treatments resulted in fragmentation of starch granules, however, they led to the clustering of the granules and formation of mucilage on their surfaces. These effects could be due to the presence of excess surface moisture that was not absorbed by starch during the modification processes (Alimi et al., 2016b).

Dimples observed on the surfaces of citric acid modified starches could be the result of weathering effect of acid hydrolysis on starch granules. Kaur, Oberoi, Sogi, and Gill (2011) similarly observed dimples on the surface of acid modified lentil starch. Atichokudomchai at al (2004) reported the erosion of tapioca starch granule surface by acid hydrolysis but without formation of pores. Difference in these observations could be due to variation in the botanical source of the starch, sizes of starch granules, type of solvent used, reaction temperature and time (Shah, Naqash, Gani, & Masoodi, 2016; Singh et al., 2007).

Source of starch and modification method did not have significant effect on the sizes of the granules (Table 1). Sizes range from 6.78 × 6.73 to 7.34 × 7.04 μm for *acha* starches and 6.35 × 7.04 to 7.47 × 7.79 μm for *iburu* starches.

3.2. X-ray diffraction

Diffraction patterns of *acha* and *iburu* starches are shown in Fig. 2. Modification did not affect the diffraction pattern of the native starches. Atichokudomchai, Varavinit, and Chinachoti (2004) also reported that acid modification did not change the diffraction spectra of tapioca starch. The retention of the native pattern after modification was reported to be due to the ordered packing of molecules within the starch structure.

Generally, the starches exhibited single prominent peaks at (2θ) 16 and 24, and a doublet at 17-19. This is a characteristic pattern of A-type crystals consistent for cereal starches (Gebre-Mariam & Schmidt, 1996; Jideani et al., 1996; Lawal et al., 2011). It was reported that side chain of amylopectin is responsible for the crystallinity of starch (Kaur, Sandhu, & Lim, 2010) and that X-ray diffraction is dependent on the chain length of amylopectin (Gebre-Mariam & Schmidt, 1996). Amylopectin with average short chain length was also reported to crystallize to A-type polymorph (Gebre-Mariam & Schmidt, 1996). Therefore, *acha* and *iburu* starches could

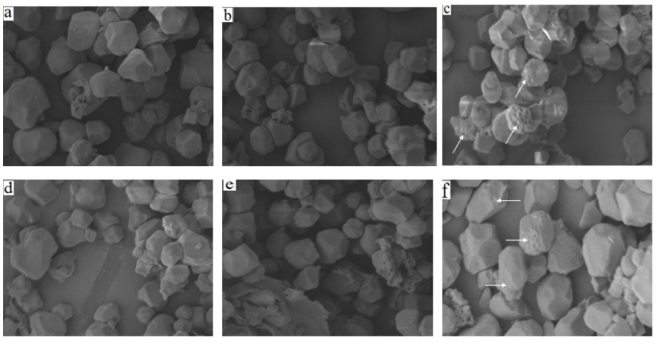

Fig. 1. Scanning electron micrographs of native and modified acha and iburu starches. (a: native acha starch; b: heat moisture treated acha starch; c: citric acid modified acha starch; d: native iburu starch; e: heat moisture treated iburu starch; e: citric acid modified iburu starch).

Table 1
Sizes of granules and crystallinity index of native and modified starches.

Sample	Length (μm)	Width (μm)	Crystallinity index[a] (%)
NAC	6.78 ± 2.28[a]	6.73 ± 2.75[a]	27.01
HAC	7.34 ± 2.29[a]	7.04 ± 1.55[a]	27.84
CAC	5.94 ± 1.16[a]	6.19 ± 1.63[a]	27.75
NIB	7.05 ± 1.99[a]	7.70 ± 2.33[a]	29.01
HIB	6.35 ± 1.35[a]	7.04 ± 1.41[a]	28.17
CIB	7.47 ± 1.89[a]	7.79 ± 1.76[a]	30.47

Mean ± SD. Mean with different superscript letters along a column are significantly different ($p < 0.05$).
NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch.
[a] Not replicated.

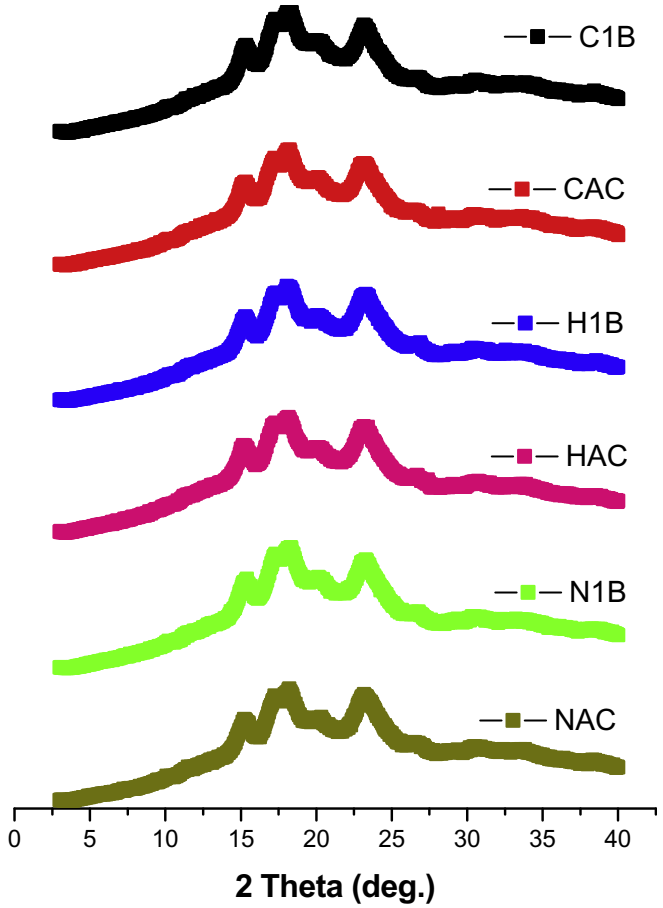

Fig. 2. X-ray diffraction of native and modified starches (NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch).

be predominated with short chain amylopectin.

Crystallinity index (CI) of the starches ranged from 27.01 to 27.84% for *acha* and 29.01 to 30.47% for *iburu* (Table 1). Heat moisture treatment had contrasting effect on the starches of the two grains. While it enhanced the CI of acha starch, it reduced that of native iburu starch. Citric acid modification increased the crystallinity of *acha* and *iburu* starches as evidenced with the increase in CI. Since starch crystallinity has direct relationship with its amylopectin content (Hizukuri, Kaneko, & Takeda, 1983), therefore, it could be inferred that weathering effect of citric acid modification led to the loss of more amylose than amylopectin and this resulted in the prominence of amylopectin molecules.

3.3. FTIR spectrometer

The FTIR spectra of native and modified *acha* and *iburu* starches are shown in Fig. 3. The FTIR spectra were used to identify types of interactions taking place within the starch matrices and possible variations that were induced by modifications. The peak transmittance bands exhibited by the starches at 3270.62 (NIB: native *iburu* starch) to 3291.30 cm^{-1} (CIB: citric acid modified *iburu* starch) correspond to OH bond stretching resonance. This is because hydroxyl groups transmit energy between 3000 and 3600 cm^{-1} wavelengths (Zhang & Han, 2006). The transmittance observed in this region indicates the contribution of water molecules to the matrices. Similar range of transmittance in this region was reported by Arueya and Oyewale (2015) for native and succinylated *acha* starches. The peak bands at 2926.74 (HAC: heat-moisture treated *acha* starch) to 2928.02 cm^{-1} (CIB) fall within the range of 2800–3000 cm^{-1} wavelength assigned for CH bonds stretching. Amylose and amylopectin contents of starch are responsible for the intensity of bands in the region. Therefore, variation in the intensities of transmittance bands observed within the region in the present study were due to differences in amylose/amylopectin contents of the starches. (Pelissari, Andrade-Mahecha, do Amaral Sobral, & Menegalli, 2013). Higher intensity implies lower amylose content and vice-versa (Kizil, Irudayaraj, & Seetharaman, 2002) From our results, citric acid modified starches of the two grains had highest band intensities and this suggested lowest amylose contents.

Peak bands observed at 1635.10 (NIB) to 1716.04 cm^{-1} (CAC) were within the region reported for amide 1 (1600-1720 cm^{-1}) by Pelissari, Andrade-Mahecha, Sobral, and Menegalli (2012). The C=O stretching of amide group of proteins were reported to be responsible for these peaks. All the starches also displayed another prominent bands at 1234.20 (CAC) to 1337.42 cm^{-1} (HIB). This bands are in the region of amide III, another protein group, which lies between 1200 and 1350 cm^{-1} (Singh, 2000). Amide III bands are products of stretching of C-N bond and inflexion of N-H bonds. These bands located within the protein groups indicated the presence of residual proteins within the starch matrices. Bands within protein group regions were also reported for plantain and banana (Pelissari et al., 2012) and *achira* flour based films (Andrade-Mahecha, Tapia-Blácido, & Menegalli, 2012). It is worth mentioning that citric acid modified starches of both grains showed two peaks in both protein groups' regions. It could be that the hydrolysis effect

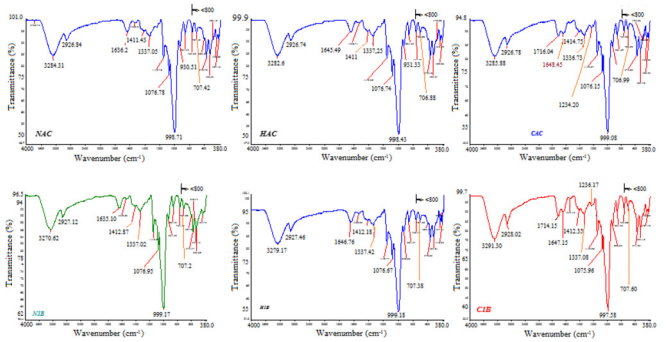

Fig. 3. FTIR of native and modified acha and iburu starches. (NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch).

of citric acid led to the erosion of some starch molecules and subsequent prominence of residual proteins in the matrices.

The bands shown by the starches at 1411 to 1414 cm^{-1} are related to the symmetric stretching of carboxyl (COO) group while the transmittance bands between 1100 and 900 cm^{-1} were the results of stretching of C-O, C-O-H and C-O-C in the glycosidic backbone of the starches (Huang, Jeng, Sain, Saville, & Hubbes, 2006; Kizil et al., 2002). The prominent bands located at 997-999 cm^{-1} gave indication to the relative differences in the crystallinity of the starches (van Soest, Tournois, de Wit, & Vliegenthart, 1995). Bands identified at 706 and 707 cm^{-1} indicate the presence of phenolic compounds in the starches (da Silva Guilarduci, de Mesquita, Martelli, & de Fátima Gorgulho, 2006). Bands within this region were also identified for banana and plantain starches by Pelissari et al. (2012).

3.4. Thermal properties of native and modified starches

The gelatinization properties of starches are shown in Table 2. Native *acha* (98.31 °C) and *iburu* (84.36 °C) starches had high peak transition temperature (T_p) of gelatinization. These values are comparable to the value of 93.5 °C reported for native *acha* starch by Emeje et al. (2012). The T_p values for the native starches of the two grains were higher than those reported for corn (65.7 °C), potato (64.4 °C), cassava (71.0 °C) and banana (74.9 °C) starches but close to the values reported for starches of some rice cultivars (81.5–88.5 °C) (Lawal et al., 2011; Pelissari et al., 2012). High T_p of gelatinization obtained in this study could be due to presence of some other components along with starch in the matrices. Zaidul et al. (2008) had earlier suggested that high T_p of gelatinization for starch could be the result of heterogeneity within the starch matrices. It should be noted that FTIR analysis of our samples indicated the presence of non-starchy components like proteins, lipid and phenolic compounds.

Modifications had opposite effect on the T_p of gelatinization of *acha* and *iburu* starches. While both modification methods led to the decrease in T_p of gelatinization for *acha* starch, they enhanced it for *iburu* starch. The differences in thermal reaction of both starches to the modification methods could be due to the different level of compactness of their granule structures, ratio of amylose to amylopectin and varying amount of non-starchy components in their matrices (Singh et al., 2007).

Generally, native and modified starches of both grains have wide gelatinization temperature range. This is similar to the trend reported for rice starches by Lawal et al. (2011). A number of factors were mentioned to be responsible for this observation. They include: large number of starch granules in unit mass, compactness, and non-homogeneity in the starch matrices (Singh & Kaur, 2004; Singh et al., 2007).

Table 2
Thermal properties of native and modified acha and iburu starches[a].

Sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔT	ΔH (J/g)
NAC	41.56	98.31	128.00	86.44	17.22
HAC	48.32	92.83	129.00	80.68	8.81
CAC	52.23	88.85	128.00	75.77	9.60
NIB	56.34	84.36	104.46	48.12	17.79
HIB	49.12	92.32	128.2	79.08	13.86
CIB	49.72	90.10	130.02	80.30	12.70

(NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch; T_o: onset temperature; T_p: peak temperature; T_c: conclusion temperature; ΔT: gelatinization temperature range; ΔH: enthalpy of gelatinization.).

[a] Not replicated.

Both methods of modification decreased the enthalpy of gelatinization of the studied starches. Similar effect of modifications on enthalpy of gelatinization were reported for banana and rice starches by Carlos-Amaya, Osorio-Diaz, Agama-Acevedo, Yee-Madeira, and Bello-Pérez (2011) and Shih and Daigle (2003), respectively. The decrease was reported to be due to the weakening of the internal network within the matrices as a result of the gaps that were created by the treatment in the double helices of amylopectin chains (Bao, Xing, Phillips, & Corke, 2003).

3.5. Pasting properties

Pasting properties of starch provide important guide to its application in food processing. Pasting properties of native and modified starches of the grains are presented in Table 3. There is no significant difference in the pasting temperature of native and heat-moisture treated starches of the grains. However, citric acid modified starches of acha and iburu remained in liquid form through the RVA pasting profile temperature cycle of heating (50-91 °C) and cooling (91-50 °C). It could be that the hydrolysis effect of acid resulted in the weakening of interactive forces within the starch granules (Alimi et al., 2016a). This position was supported by earlier report that acid modification caused partial debranching of amylopectin molecules thereby weakening the internal cohesion within starch matrices. The resultant effect was the thinning of starch granules (Kaur, Gill, & Sogi, 2007).

Both modification methods employed led to reduction in pasting viscosities of *acha* and *iburu* starches. The effect was more pronounced in acid modified samples. Similar observation was reported by Ferrini, Rocha, Demiate, and Franco (2008) in their study on the effect of acid treatment on cassava and maize starches. The decrease in pasting viscosities was higher in *iburu* starch. The extent of decrease in viscosities with acid modification suggest the ease of polymerization of the starches by the treatment. Very low setback viscosities obtained for the CAM starches confirmed previous report that acid modification led to reduction in retrogradation tendency of starch (Shah et al., 2016).

3.6. Color parameters

The CIE L^*, a^*, b^* color parameters of native and modified *acha* and *iburu* starches are shown in Table 4. Native *acha* starch was lighter (88.96) than native *iburu* starch (83.53). Both modification methods enhanced the lightness of the grains' starches. Falade and Ayetigbo (2015) had earlier reported increase in lightness intensity with citric acid modification of yam cultivars. Since presence of impurities like residual phenolic compounds, protein and lipids were reported to be responsible for decrease of L^* index of starch (Ali, Falade, & Akingbala, 2012), it could be explained that partial removal or purification of these impurities by the treatments were responsible for the higher L^* index values obtained for modified starches. The implication is that HMT and CAM treatments of these starches could make them good candidates in clear starchy products. All starch samples had low tones of redness, a^*, (-0.28 to 0.66) and yellowness, b^*, (5.09–8.18). *Acha* starches were generally whiter than the corresponding *iburu* starches as shown by their higher whiteness (W) values. Modifications did not have significant effect ($p < 0.5$) on color intensity (ΔE) of the starches from the two grains. The implication is the uniformity of color within cultivar (Pelissari et al., 2012). This uniformity in ΔE values recommends the starches for use in such materials where uniformity of color is of essence. Examples include ice creams, juices and candies. However, except for NAC, *iburu* starches generally have significantly ($p < 0.05$) higher ΔE than *acha* starches. This fact and the higher

Table 3
Pasting properties of native and modified acha and iburu starches.

Sample	Pasting temperature (°C)	PV (cP)	Peak time (min)	Trough (cP)	FV (cP)	BV (cP)	SBV (cP)
NAC	75.78 ± 0.04^{b}	5063.50 ± 4.95^{d}	5.27 ± 0.00^{c}	3025.50 ± 10.61^{d}	4252.50 ± 2.12^{e}	2038.00 ± 5.66^{e}	1227.00 ± 12.73^{e}
HAC	76.20 ± 0.57^{bc}	4941.50 ± 9.19^{c}	5.27 ± 0.00^{c}	2997.50 ± 14.85^{d}	4180.50 ± 36.06^{d}	1944.00 ± 24.04^{d}	1183.00 ± 21.21^{d}
CAC	NR	33.00 ± 0.00^{a}	4.74 ± 0.09^{b}	17.50 ± 0.71^{a}	37.00 ± 0.00^{a}	15.50 ± 0.71^{a}	19.50 ± 0.71^{a}
NIB	76.58 ± 0.04^{c}	4181.00 ± 16.97^{b}	5.50 ± 0.04^{d}	2564.00 ± 26.87^{b}	3534.50 ± 9.19^{c}	1617.000 ± 9.90^{c}	970.50 ± 17.68^{c}
HIB	76.55 ± 0.07^{c}	4136.00 ± 73.54^{b}	5.44 ± 0.05^{d}	2634.50 ± 26.16^{c}	3464.00 ± 33.94^{b}	1501.00 ± 49.49^{b}	829.50 ± 7.78^{b}
CIB	NR	16.50 ± 2.12^{a}	4.47 ± 0.00^{a}	7.50 ± 0.71^{a}	18.50 ± 0.71^{a}	8.00 ± 0.00^{a}	11.00 ± 0.00^{a}

Mean ± SD. Mean with different superscript letters along a column are significantly different ($p < 0.05$).
(PV: peak viscosity; FV: final viscosity; BV; breakdown viscosity; SBV: setback viscosity; NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch; NR: no reading).

Table 4
CIE Color parameters of the starches.

Sample	L^*	a^*	b^*	H	W	ΔE
NAC	88.96 ± 5.11^{a}	-0.28 ± 0.01^{a}	6.85 ± 0.88^{ab}	92.33 ± 0.10^{b}	86.93 ± 4.78^{ab}	18.99 ± 5.18^{ab}
HAC	93.46 ± 1.32^{b}	0.30 ± 0.78^{a}	5.78 ± 1.26^{a}	87.90 ± 7.33^{b}	91.25 ± 1.85^{b}	14.45 ± 1.49^{a}
CAC	93.80 ± 2.11^{b}	0.66 ± 0.27^{b}	5.09 ± 1.43^{a}	82.74 ± 0.98^{ab}	91.95 ± 2.55^{b}	14.09 ± 2.29^{a}
NIB	83.53 ± 1.87^{a}	0.37 ± 0.03^{ab}	9.25 ± 0.13^{c}	87.72 ± 0.18^{b}	81.10 ± 1.57^{a}	24.76 ± 1.81^{b}
HIB	85.62 ± 3.46^{a}	0.19 ± 0.11^{a}	8.18 ± 0.50^{bc}	88.69 ± 0.83^{b}	83.38 ± 2.75^{a}	22.52 ± 3.32^{b}
CIB	84.86 ± 0.01^{a}	2.26 ± 0.11^{b}	6.31 ± 0.15^{ab}	74.32 ± 6.06^{a}	83.44 ± 0.06^{a}	23.19 ± 0.01^{b}

Mean ± SD. Mean with different superscript letters along a column are significantly different ($p < 0.05$).
(NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch; L^*: lightness index; a^*: redness index; b^*: yellowness index: H: Hue angle, ΔE: color intensity; W: degree of whiteness).

L^* and W values of *acha* starches could place *acha* starches above *iburu* starches where clear starchy products are desired.

3.7. Functional properties

Functional properties of the starches are shown in Table 5. There is no significant difference in the water absorption capacity (WAC) of the native starches of the two grains. Heat moisture treatment had contrasting effect on the WAC of *acha* and *iburu* starches. While the treatment led to reduction in the WAC of *acha* starch, it increased that of *iburu*. However, similar to the report of Kaur et al. (2011), CAM generally led to decrease in WAC of the starches of the two grains. Water absorption capacity of starch is a function of the comparative quantity of amylose and amylopectin and their relative association in the starch granules. Relatively higher WAC implies lower amylopectin content (Alimi et al., 2016b) and by implication, lower degree of starch crystallinity (Kaur et al., 2011). It therefore followed that WAC is inversely related to the degree of crystallinity in the starch granules. This trend was established in this study. The trend of WAC was opposite to that of CI for our starch samples.

Oil absorption capacity (OAC) of the starches showed trends similar to WAC. Varietal difference could be responsible for the different effect of HMT on *acha* and *iburu* starches (Alimi et al., 2016a). There was general decrease in OAC with CAM. This could be due to the thinning effect of acid modification. The thinning effect was reported by Kaur et al. (2011) to enhance lipophobic tendency of starch.

While HMT increased alkaline water retention (AWR) of *acha* and *iburu* starches, CAM led to its reduction in the starches of both grains. The information of AWR of the starches will provide a useful guide in their application under alkaline/basic processing condition.

Emulsifying capacity (EC) and relative occluded volume (ROV) are indices of oil-water interaction of starches. There is no significant ($p < 0.5$) difference in the EC and ROV among the starches.

Native *acha* starch had higher gelling capability (6%) than native *iburu* starch (8%). Hydrothermal modification did not affect the gelation capability of the two starches. However, CAM treated starches did not gel throughout the starch increment range. Ferrini et al. (2008) also reported significant drop in the viscosity forming ability of cassava and maize starches that were treated with acid-methanol. This result was reported to be due to the attack of amylopectin molecules located in the amorphous region of the starch granules by acid.

Table 5
Functional properties of acha and iburu starches.

Sample	WAC	OAC	AWR	EC	ROV	LGC	
						Soft gel	Firm gel
NAC	1.80 ± 1.18^{a}	2.40 ± 0.05^{a}	0.91 ± 0.06^{ab}	0.45 ± 0.01^{a}	0.82 ± 0.03^{a}	6	12
HAC	1.54 ± 0.40^{a}	2.14 ± 0.05^{a}	0.97 ± 0.04^{b}	0.44 ± 0.01^{a}	0.80 ± 0.04^{a}	6	10
CAC	1.36 ± 0.26^{a}	2.16 ± 0.02^{a}	0.55 ± 0.08^{a}	0.46 ± 0.02^{a}	0.86 ± 0.08^{a}	Nil	Nil
NIB	1.64 ± 0.44^{a}	2.27 ± 0.11^{a}	0.97 ± 0.00^{b}	0.46 ± 0.02^{a}	0.87 ± 0.07^{a}	8	12
HIB	1.96 ± 0.68^{a}	2.80 ± 1.29^{a}	0.97 ± 0.01^{b}	0.45 ± 0.02^{a}	0.83 ± 0.07^{a}	8	12
CIB	1.17 ± 0.49^{a}	2.23 ± 0.24^{a}	0.90 ± 0.02^{a}	0.44 ± 0.05^{a}	0.80 ± 0.16^{a}	Nil	Nil

Mean ± SD. Mean with different superscript letters along a column are significantly different ($p < 0.05$).
(NAC: native acha starch; HAC: heat moisture treated acha starch; CAC: citric acid modified acha starch; NIB: native iburu starch; HIB: heat moisture treated iburu starch; CIB: citric acid modified iburu starch: WAC: water absorption capacity: OAC: oil absorption capacity: AWR: alkaline water retention; EC: emulsion capacity; ROV: relative occluded volume; LGC: least gelation concentration).

4. Conclusion

Heat moisture treatment and citric acid modification had varying effects on the studied properties of *acha* and *iburu* starches. They both led to the clustering of starch granules and mucilage formation while only CAM resulted in dimple formation on the surface of the granules. None of the modification methods affected sizes of the granules and the type-A diffraction pattern of the native starches. Results of FTIR spectrophotometry and thermal analysis suggested heterogeneity of the starch crystals. Decreased viscosities as a result of polymerization of starches by citric acid are important quality factors that could promote their applications in imitation cheese, candies and processed meats. Acid modified starches are also known to produce better quality plastic films than native starches. Relative safety of the treatments to human health is an added advantage for their applications in food and pharmaceutical. Enhanced lightness and whiteness indices that resulted from HMT and CAM treatments put the starches from the two grains as important candidates in products where color clarity is of essence. Examples include ice-creams, juices, candies and tablet excipient. The abovementioned and other quality changes induced by the treatments position *acha* and *iburu* as potential cheap starch sources for varying food and pharmaceutical applications.

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