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Thermal Treatment Effects on the Calcium Oxalate and Mineral Contents of *Xanthosoma Atrovirens (ede ocha)*: a Cocoyam Species

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Abstract
The extent to which the irritant in cocoyam can be destroyed and removed during thermal treatment and the resultant effect of the treatment on the mineral content and influence of tuber thickness are investigated in this study. Wholesome tubers of cocoyam (*Xanthosoma atrovirens*) were selected and subsequently cleaned, peeled, washed and size reduced into various dimensions (1cm, 3cm and 5cm thickness). The various dimensions were subjected to boiling and samples were withdrawn at intervals of 0, 30, 60, 90 and 120 min. The boiled samples were further sliced into smaller sizes; dried in an air- oven at a temperature of 55°C to a constant weight, milled into flour and packed in polythene material and stored in dry condition. The design of the study fitted into 3 (dimension) x 5 (boiling duration) factors. The flours generated were subjected to calcium oxalate and mineral loss or gain analyses. Significant reduction in calcium oxalate occurred at $p< 0.05$ as the boiling time interval increased. The highest removal of calcium oxalate occurred for the 1.0 cm thickness in which the acrid taste was found to disappear after boiling for 60 min. However the oxalate in the 3.0 cm and 5.0cm thickness were found to disappear after boiling for 120 min. Similarly, mineral losses were significant at intervals of boiling time used for the study. The 1.0 cm thickness showed the highest loss of potassium from the initial value of 1099.27mg/100g flour at 0.0 min to 586.77mg/100g after 120 min. The 3.0 cm, with the initial potassium value 1100.30 mg/100g was reduced to a value of 598.20 µg/100g after 120 min boiling, while the 5.0 cm thickness had potassium value reduced to 607.97 mg/100g at 120 min boiling from the initial potassium value of and 1101.77mg/100g. Also, reductions in minerals were observed for magnesium, phosphorus and calcium. Tuber thickness and boiling duration are the controlling factors in calcium oxalate and mineral loss. It might be recommended that cocoyam be cut to size thickness of 1.0cm since it gave reduced time of cooking of 60 min which resulted to the disappearance of calcium oxalate in the cooked material and energy saving..
Keywords: *Xanthosoma Atrovirens*; tuber thickness; boiling time; calcium oxalate; mineral loss.

Introduction

Aroids make significant contribution both as root crops and vegetables in the diets of people particularly in rural areas where they are freely available. However the aroids are yet to realize there full potentials because of the palatability problems associated with their high content of oxalate in form of raphides (Hussian et al., 1984; Iwuoha and Kalu, 1995). Cocoyams contribute remarkably to the carbohydrate diet for diabetics and production of weaning food for infants and for those with gastrointestinal disorders (Onwuneme, 1978; Obomeghei et al.,1998; FAO, 2006).

Most Aroids contain calcium oxalate (raphides) in their corms, cornels and leaves, which appear microscopically as small-cigar shaped capsules of gelatin–like nature open at one end; which when wetted eject crystalline spears or raphides into the surrounding tissues. The exact chemical form is calcium oxalate which has acidic taste and on contact with the skin; mouth or throat causes prickly feeling (irritation) within a few seconds. These raphides, if consumed in large quantity may cause kidney damage, and also interferes with the assimilation of calcium, magnesium, iron and copper (FAO, 2006).

Fagbemi and Olaofe (1998) stated that dietary oxalate has been known to complex with calcium, magnesium and iron leading to the formation of insoluble oxalate salts and resulting in oxalate stone.

Sakai (1979) reported that no human death has been linked to the eating of uncooked ariods, however numerous research works have shown that experimental and domestic animals have died during feeding trials.

This calcium oxalate crystals can be removed or broken down by proper heat treatment (Hussian, et al., 1984). The heat treatment breaks up the bonds and the freed calcium becomes soluble. This is why after thorough cooking or boiling, cocoyam can be eaten without itching effect especially when properly prepared or heat treated (Ukpabi and Ejidoh, 1989).

Effective removal of the calcium oxalate will enhance the utilization of cocoyam flour in food formulations such as flour for biscuit making, pie filling, binder in sausage etc.(Obomeghei, et al., 1998).

The present study evaluates the boiling regime as well as the influence of tuber thickness on the effective

elimination of calcium oxalate and mineral losses in the resultant cocoyam flour.

MATERIALS AND METHODS

Materials

The cocoyam species used for the study was purchased from Eke ukwu Owerri market on 21th June, 2012 and was conveyed to National Root Crop Research Institute (NRCRI) Umudike, Umuahia, where it was identified as ede ocha (*Xanthosoma atrovirens).* The cocoyam was sorted to separate healthy tubers from rot infested ones. Only healthy tubers were selected for the study. These were subsequently cleaned, peeled, washed and size reduced into various dimensions (1cm, 3cm and 5cm thickness). The various dimensions were subjected to boiling and samples withdrawn at intervals of 0, 30, 60, 90 and 120 min. The boiled samples were further sliced into smaller sizes; dried in an air- oven at a temperature 55°C to a constant weight, milled into flour and packed in a moisture proof polythene material. The design of the study fitted into 3 (dimension) x 5 (boiling duration) factors.

The flours generated were subjected to oxalate determination and mineral loss or gain due to thermal treatment.

Determination of oxalate by titrametric method.

The method described by (Onwuka, 2005) was followed. The procedure involves three (3) steps: digestion, oxalate precipitation and permanganate titration

Digestion

Two (2) grammes of cocoyam flour were weighed out and dissolved in 190ml of distilled water in a 250ml volumetric flask. 10ml of 6N HCl was added to digest the mixture, which was maintained at 100°C for 1.0 h. This was allowed to cool and thereafter made up to 250ml with distilled water and filtered.

(ii) Oxalate precipitation

Triplicate portions of 125mL aliquot of the filtrate were measured into beaker and four drops of methyl red indicator added, followed by the addition of conc. NH_4OH solution drop wise until the solution changed from its salmon pink colour to a faint yellow colour (pH 4 - 4.5). Each mixture was then heated up to 90°C, cooled and filtered to remove precipitate containing ferrous ion. Each was again heated to 90°C and 10mL of 5% $CaCl_2$ solution added with constant stirring, and left over-night in the chiller at a temperature of 5°C.

Permanganate titration:

After being allowed to stand for 12 h, the solution was then centrifuged at 2,500 rpm for 5 min. The supernatant was decanted again and the precipitate completely dissolved in 10mL of 20% (v/v) H_2SO_4. The solution was heated until it almost attained boiling, and then titrated against 0.05N standardized $KMnO_4$ solution to a faint pink colour that persists for 30s.

Calculation:

The Calcium oxalate content was calculated based on equivalent amount of $KMnO_4$ solution used for the titration, where: 1mL of 0.05N $KMnO_4$ solution is equivalent to 0.00225g anhydrous oxalic acid, and using the expression:

$$\frac{T \times (Vme)\ (Df) \times 10^5}{(ME) \times Mf}\ (mg/100g)$$

Where: T is the titre of $KMnO_4$ (ml); Vme is the volume-mass equivalent (i.e. 1mL of 0.05N $KMnO_4$ solution is equivalent to 0.00225g anhydrous oxalic acid); Df is the dilution factor V_T/A (2.4 where V_T is the total volume of titrate (300mL) and A is the aliquot used (125mL); ME is the molar equivalent of $KMnO_4$ to oxalate ($KMnO_4$ redox reaction) and; Mf is the mass of flour used.

Mineral content determination

Mineral contents of (calcium, potassium, Magnesium and phosphorus) of ede ocha was determined by atomic absorption spectrophotometry. One gramme of dried sample was ashed in a Muffle furnace (model SXL) at 700°C for 4 hours, and thereafter allowed to cool to room temperature. The ashed sample was leached with 5 ml of 6N HCl , and the volume was made up to 50 ml with deionised water.

The determination of calcium and magnesium in the sample was done using an atomic absorption spectrophotometer (model- UNICAM 939/959 atomic absorption spectrometer), by direct aspiration of sample into air-acetylene flame, at a set wavelength of 422.7 nm. Calcium carbonate, potassium chloride, magnesium oxide and monophosphate respectively were used as standard to prepare the calibration curve within the analytical range (Siong et al.,1989) The absorbance was measured in triplicate for each sample and the average value reported.

Statistical Analysis

The data from the study obtained in triplicates, were subjected to analysis of variance (ANOVA) using the SAS software (SAS 2000).

RESULTS AND DISCUSSION

Influence of Boiling Time and Tuber Thickness on Calcium Oxalate Content of ede-ocha (*Xanthosoma atrovirens*).

Table 4.1 shows the effect of boiling and tuber thickness (1.0 cm, 3.0cm and 5.0 cm) on reduction of calcium oxalate in *Xanthosoma atrovirens* tuber. There were significant reductions ($p < 0.05$) in the oxalate values as the boiling time increased for the various sample thickness. Quantitatively, more oxalate loss occurred for the 1.0 cm size thickness in which the oxalate was found to disappear after 60 min of boiling. The oxalate in the 1.0 cm sample was found to decrease to 279.20 mg/100g flour in the first 30 min of boiling which translate to 54.7 % loss. And at the 60 min of boiling, the calcium oxalate value stood out 118.60mg/100g sample and represents 57.52% loss. However for the 3.0 cm thickness, calcium oxalate loss was lower than that of 1.0 cm thickness, the calcium oxalate remaining after 30min of boiling was 326.18 mg/ 100g flour, which showed that 47% loss occurred. Similarly for the 5.0cm thickness the oxalate was found to disappear after boiling for 120 min. Although the amounts of oxalate removed were higher for 3.0 cm and 5.0 cm as shown by values obtained after boiling for 90 min (16.50 and 59.30 mg/100g flour for 3.0 and 5.0cm respectively). A clear inference might be drawn from the above observations that the extent of boiling and tuber thickness is the controlling factors for calcium oxalate removal in cocoyam. Heat destroys raphide structure and the result obtained in the study agrees with earlier reports that cooking/boiling enhances the destruction of the acrid factor in cocoyam (Sakai, 1979; Onwueme, 1978; Ihekoronye and Ngoddy, 1985). The raphides containing cells rupture upon strong heating, releases the raphides which remains in the idioblast cells; although they remain unchanged but become harmless (Sakai, 1979).

Table 1.0 mean values of Calcium Oxalate of Ede-Ocha (*Xanthosoma Atrovirens*) as affected by boiling time and tuber Thickness on

Boiling Time (min)	Loss/Ca oxalate content (mg/100g flour) of various size thickness		
	1cm	3cm	5cm
0	615.70^{a}±0.42 (54.7%)	616.30^{a}±0.31 (47%)	617.90^{a}±0.09 (46.1%)
30	279.20^{b} ±1.30 (57.5%)	326.18^{b}±1.46 (47%)	332.50^{b}±1.90 (41.7%)
60	118.60^{c}±0.61	173.10^{c}±0.14 (90.5%)	193.80^{c}±1.40 (69.9%)
90	NA	16.50^{d}±0.93	59.30^{d}±4..50
120	NA	NA	NA

Means are triplicate determinations, means with similar letters of alphabet along the column did not differ significantly at $p>0.05$. NA =not available. values in parenthesis are the percent loss of calcium oxalate.

The mechanism of raphides release from the idioblast cell of the disrupted plant material involves swelling of polysaccharide material within the idoblast cell (which contains a large array of raphides arranged like shealth of arrows) (Sakai and Hanson, 1974).

Influence of boiling time and tuber thickness on potassium loss (mg/100g) of ede ocha (*Xanthosoma atrovirens)*

Table 2.0, shows how boiling time and tuber thickness affected the potassium content of ede ocha (*Xanthosoma atrovirens)*. The 1.0 cm thickness showed the highest loss of potassium from the initial value of 1099.27mg/100g flour at 0.0 min to 586.77mg/100g after 120 min. The 3.0 cm, with the initial potassium value 1100.30mg/100g was reduced to a value of 598.20 mg/100g after 120 min boiling, while the 5.0 cm thickness had potassium value reduced to 607.97 mg/100g at 120 min boiling from the initial potassium value of and 1101.77 mg/100g. Gradual loss of potassium occurred from 0.0 min to 30 min of boiling (representing 13.7%, 13.2% and 12.8% for 1.0cm, 3.0cm and 5.0cm thickness respectively).but greater losses occurred from 60 to 120 min boiling, suggesting that more mineral loss occurred after the first 30 min of boiling. The observed general trend is that as the boiling regime increases more minerals are leached out from the tuber matrix into the boiling medium. These findings corroborates earlier report by Bradbury and Holloway, (1988) that the rate of nutrient loss during cooking is a function of time and cooking method employed. Ihekoronye and Ngoddy (1985) and Hotz and Gibson (2007) also reported that nutrient or mineral losses during boiling are due to leaching, oxidation of water soluble minerals and thermal destruction. When tubers e.g. yam, cocoyam etc are boiled, the dietary fibre content rises because starches are modified and some minerals are lost particularly potassium (Fagbemi and Olaofe, 1998).

Potassium is crucial for proper heart function and plays a key role in skeletal and smooth muscle contraction, making it important for normal digestive and muscular function, too (Myers, 2007; Lanham-New, 2008).

Table 2.0 mean values of Potassium (mg/100g of flour) in Ede-Ocha (*Xanthosoma Atrovirens*) as affected by boiling time and tuber thickness.

Boiling Time (min)	Potassium content (mg/100g of flour) for various tuber Thickness		
	1cm	3cm	5cm
0	1099.27^{a} ± 85.31 (13.7%)	1100.30^{a} ± 85.67 (13.2%)	1101.77^{a} ± 85.46 (12.8)
30	948.90^{b} ±85.69 (15.1%)	954.63^{b} ± 85.67 (14,6%)	960.67^{b} ± 87.05 (14.5)
60	805.30^{c} ± 77.25 (13.1%)	815.17^{c} ± 77.54 (13%)	821.67^{c} ± 77.10 (13%)
90	700.27^{d}± 74.22 (16.2%)	709.53^{d} ± 75.24 (15.7%)	715.00^{d} ± 76.19 (14.9%)
120	586.77^{e} ± 74.18	598.20^{e} ± 77.29	607.97^{e} ± 77.73
LSD	14.04	13.89	15.03

Means are triplicate determinations, means with similar letters of alphabet along the column did not differ significantly at p>0.05. values in parenthesis are the percent loss of potassium.

Influence of boiling time and tuber thickness on magnesium loss (mg/100g) of ede ocha (*Xanthosoma atrovirens)*

Losses in magnesium was observed in Table 3, where greatest reduction occurred in 1.0 cm of ede ocha tuber as 65.51, 55.00, 45.47, 35.83, 27.74mg/100g for 0.0, 30, 60, 90 and 120 min respectively. The 3.0 cm thickness was reduced to 30.87 mg/100g from the initial 65.97 mg/100g at 0.0 min after boiling for 120 min, while for the 5.0 cm thickness; magnesium content was reduced to 34.57 mg/100g for 120 min boiling from 66.27 mg/100g at 0.0 min. The lesser the thickness, the more ease of leaching of the mineral content.

Magnesium helps in the regulation of blood sugar levels, promotes normal blood pressure, and is known to be involved in energy metabolism and protein synthesis (Rude and Olerich, 1996). Firoz and Graber (2001) stated that there is an increasing interest in the role of magnesium in prevention and management of disorders such as hypertension, cardiovascular disease, obesity and diabetes.

Table 3.0 mean values of magnesium (mg/100g of flour) in Ede-Ocha (*Xanthosoma Atrovirens*) as affected by boiling time and tuber thickness.

Boiling Time (min)	magnesium content (mg/100g of flour) for various tuber Thickness		
	1cm	3cm	5cm
0.0	65.51^{a} ± 3.75 (15.4%)	65.97^{a} ± 3.84 (14.2%)	66.27^{a} ± 3.76 (11.5%)
30	55.00 ^{b}± 4.30 (17.3%)	56.63^{b} ± 3.68 (15.0%)	58.67^{b} ± 3.76 (13.6%)
60	45.47^{c} ± 4.33 (18.9%)	48.13^{c} ± 3.68 (17.7%)	50.70 ^{c} ± 3.77 (15.9%)
90	35.83 ^{d}± 4.65 (20.8%)	39.63^{d} ± 3.68 (22.1%)	42.60^{d} ± 3.78 (18.5%)
120	27.74^{e} ± 4.66	30.87^{e} ± 3.72	34.57^{e} ± 3.78
$LSD_{0.05}$	2.61	6.00	3.78

Means are triplicate determinations, means with similar letters of alphabets along the column did not differ significantly at p>0.05. values in parenthesis are the percent loss of magnesium.

The loss of phosphorus (mg /100g flour) in ede ocha (*Xanthosoma atrovirens)* as affected by boiling time and tuber thickness.

The losses in phosphorus content during boiling are shown in Table 4. There significant differences ($p < 0.05$) in the amount of retained phosphorus at every interval of time. More of the mineral losses occurred in the 1.0 cm thickness, followed by 3.0 cm and 5.0 cm. The residual values at 120 min of boiling were as follows: 27.33, 32.37 and 37.07mg/100g for 1.0, 3.0 and 5.0 cm respectively from initial values of 55.30, 50.28 and 53.43 mg/100g flour. It is revealed that significant losses of phosphorus loss occurred as the boiling time increased for the various tuber thicknesses. The least residual phosphorus obtained for 1.0 cm thickness is because of the large surface exposed to the heating and cooking water. Phosphorus helps filter out waste in the kidneys and plays an essential role in how the body stores and uses energy. It also helps to reduce muscle pain after a hard workout, and it is needed for growth, maintenance and repairs of all tissues and cells. Phosphorus plays important roles in the production of the genetic building blocks, DNA and RNA; and also needed to balance and promote

utilization of other minerals and vitamins, including vitamin D, iodine, magnesium and zinc (Elliot et al., 2008).

Table 4.0 mean values of Phosphorus (mg/100g of flour) in Ede-Ocha (*Xanthosoma Atrovirens*) as affected by boiling time and tuber thickness.

Boiling Time (min)	phosphorus content (mg/100g of flour) for various tuber Thickness		
	1cm	3cm	5cm
0.0	$55.30^{a} \pm 4.70$ (12.8%)	$56.11^{a} \pm 5.47$ (10.4%)	$57.20^{a} \pm 5.78$ (6.6%)
30	$48.20^{ab} \pm 4.70$ (12,2%)	$50.28^{b} \pm 5.47$ (10.3%)	$53.43^{b} \pm 5.28$ (10.3%)
60	$42.30^{b} \pm 4.60$ (18.4%)	$44.47^{c} \pm 5.27$ (11.3%)	$47.93^{c} \pm 5.28$ (11.3)
90	$34.50^{c} \pm 4.86$ (20.8%)	$38.55^{d} \pm 5.25$ (12.8%)	$42.53^{d} \pm 5.28$ (12.8%)
120	$27.33^{d} \pm 4.50$	$32.37^{e} \pm 5.24$	$37.07^{e} \pm 5.44$
$LSD_{0.05}$	7.16	3.64	3.58

Means are triplicate determinations, means with similar letters of alphabets along the column did not differ significantly at p>0.05. values in parenthesis are the percent loss of phosporus

Influences of boiling time and tuber thickness on calcium loss (mg /100g) of ede ocha (*Xanthosoma atrovirens)*

Table 5 shows the leaching out of calcium as the boiling duration increased for the various tuber thicknesses. As were observed for the other minerals, the loss of calcium was significant ($p< 0.05$) for the various boiling time. The calcium losses were gradual for the first 30 min of boiling but the rate increased from 60 min to 120 min of boiling. At the end of boiling for 120 min, 34.50% of calcium was retained in 1.0 cm (13.66mg/100g), 44.16% in 3.0 cm (17.71 mg/100g) and 50.68 % in 5.0 cm (20.61 mg/100g) respectively. It is revealed that the heat destruction of calcium oxalate raphide did not translate to increase in calcium content of the flour. Sakai (1979) reported that the raphides though destroyed are held to the idioblast cell. Calcium is essential for proper blood clothing and most dietary calcium are absorbed in the small intestine and transported in the blood stream (Olendorf et al., 1999). Calcium stored in bone can be used to maintain adequate blood calcium levels, short-term dietary deficiency of calcium generally does not result in significantly low blood calcium levels but over the long term, dietary deficiency eventually depletes bone stores, rendering the bones weak and prone to fracture

Table 5.0 mean values of calcium (mg/100g of flour) in Ede-Ocha (*Xanthosoma Atrovirens*) as affected by boiling time and tuber thickness.

Boiling Time (min)	calcium content (mg/100g of flour) for various tuber Thickness		
	1cm	3cm	5cm
0.0	$39.53^{a} \pm 3.76$ (17.3%)	$40.10^{a} \pm 3.67$ (13.4%)	$40.67^{a} \pm 3.56$ (12.2%)
30	$32.70^{b} \pm 3.73$ (20.1%)	$34.71^{b} \pm 3.77$ (16.5%)	$35.69^{b} \pm 3.56$ (14.3%)
60	$25.90^{c} \pm 3.73$ (18.2%)	$28.97^{c} \pm 3.78$ (19.4%)	$30.58^{c} \pm 3.57$ (16.2%)
90	$21.19^{d} \pm 3.60$ (33.6%)	$23.34^{d} \pm 3.79$ (24.1%)	$25.63^{d} \pm 3.62$ (19.6%)
120	$13.66^{e} \pm 3.70$	$17.71^{e} \pm 3.80$	$20.61^{e} \pm 3.64$
$LSD_{0.05}$	2.83	2.53	3.68

Means are triplicate determinations, means with letters of alphabets along the column did not differ significantly at p>0.05.values in parenthesis are the percent loss of calcium.

CONCLUSION

The study revealed that boiling effectively destroys calcium oxalate raphide in cocoyam. The extent of the destruction calcium oxalate raphide was influenced by boiling duration and the thickness of the tuber. Smaller size of tuber cuts guaranteed high removal of oxalate and reduction of cooking time.

On the other hand, thermal treatment (boiling) resulted to losses in mineral content by softening the plant tissue, which aided the leaching out of the minerals from ede-ocha (e.g. potassium, magnesium, phosphorus and calcium) as the cooking time increased. Generally the rate of mineral losses in the 1cm size (thickness) was higher when compared to those of 3cm and 5cm cooked at same interval of time.

The doneness of the various thickness of the cocoyam tubers might necessarily be associated with the time for

the disappearance of calcium oxalate, which were 60 min for 1cm cut and 120 min for both 3cm and 5cm cuts. Therefore, tuber thickness and boiling duration are essential factors for the removal calcium oxalate; these also influence the mineral losses.

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