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Varietal Changes in Proximate Composition and the Effect of Processing on the Ascorbic Acid Content of Some Nigerian Vegetables

[1]Olumuyiwa S. Falade, [2]A. F. Dare, [3]Muibat O. Bello, [4]Bolanle O. Osuntogun and [1]Steve R. A. Adewusi
[1]Department of Chemistry; [2]Home Economics Unit, Department of Agricultural Extension and Rural Sociology, Obafemi Awolowo University, Ile-Ife, Nigeria; [3]Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, P.M.B. 4000, Ogbomosho, Nigeria
[4]Department of Chemistry, University of Lagos, Akoka, Lagos, Nigeria

Abstract: The proximate composition of some varieties of commonly eaten vegetables in Nigeria was determined and some processing and storage methods evaluated using ascorbic acid as an index. The local variety of *A. viridis* contained a higher level of ash, crude fibre, ascorbic acid and lipid content compared to the exotic green variety while the green *C. argentea* vegetable has a statistically higher content of crude protein, ash, ascorbic acid and less of crude fibre and total carbohydrate compared to the purple variety to justify the introduction of the exotic green variety of *C. argentea*. Blanching *Vernonia amygdalina* and *Struchium spargonophora* in hot water reduced the ascorbic acid by 12-13% while maceration to remove the bitter taste reduced it by 96%; increased the tannin content in *Struchium* (14%) but increased the oxalate level by 25% in *Vernonia*. There was a 27% decrease in the ascorbic acid content of fresh *Amaranthus* and *Struchium* over the 288 h storage period in the freezer compared to a loss of 47 - 67% for the blanched samples. The sun and oven dried materials lost all their ascorbic acid content during the storage period at room temperature with 88 - 97% loss within the first 48 h.

Key words: Proximate, composition, ascorbic acid, nigerian, vegetables

Introduction

Protein malnutrition (kwashiorkwor in children) is still prevalent in the developing countries of the world as a result of the high cost of animal protein, ignorance about the nutritional quality of foods and taboos which forbid the consumption of certain nutritious foods in specific environments. A case had been made for the use of protein from locally produced vegetable to combat malnutrition (Oke, 1975 and Lucas, 1988). Several types of exotic vegetable as well as new lines or varieties of existing vegetables have been introduced into Nigeria for its potherb qualities or grain production (Ologunde *et al.*, 1992).

A typical example is that of the most popular potherb vegetable in Nigeria - *Amaranthus viridis*, which has many varieties and probably many more hybrids. Two varieties of Amaranthus are widely grown in Nigeria - the luscious green variety, which was introduced several years ago and the local variety. *Celosia argentea*, another widely consumed vegetable in south western Nigeria, also exists in green and purple varieties. All varieties are consumed without regard to their nutritional constituents and in many cases, the scientific information is lacking.

In addition to the high protein content, vegetables are also good sources of minerals, vitamins (Adewusi and Bradbury, 1993; Awoyinka *et al.*, 1995; Rangaranjan and Kelly, 1998 and Rangaranjan *et al.*, 1998) and dietary fiber which reduces blood cholesterol and sugar levels in the affluent few (Brown *et al.*, 1999 and Fakoya *et al.*, 1997).

Green vegetables are normally difficult to preserve. The best method of preservation is freezing, which has been reported to cause a reduction in the level of ascorbic acid (Lee and Labuza, 1975). Other methods of preservation include blanching and sun drying especially in the local communities where electricity and freezers do not exist. The ascorbic acid content of some Nigerian vegetables has been reported (Achinewhu, 1983) but information on the content of this important vitamin in different varieties of vegetables and its stability during processing is limited or lacking. The purpose of this study was to determine the proximate composition of commonly eaten vegetables in Nigeria and to evaluate the rate of deterioration of two selected vegetables using ascorbic acid as an index.

Materials and Methods

The vegetables were bought in the local market in Ile-Ife, cleaned of dirt and foreign matter, diced and washed with distilled water. Samples for moisture determination were not washed. A portion of the vegetables was blanched with hot water as described earlier (Falade *et al.*, 2003). Two vegetables with the lowest and highest ascorbic acid content were selected and studied for the effect of processing on the vitamin content. Five-gram portions of fresh and blanched vegetables were weighed into polythene bags or sample bottles / containers and kept in the freezer at -18°C. Vegetable samples were sun dried (Temp. 38-42°C) for 48 hours to mimic the local procedure in communities without electricity or the means to purchase a refrigerator. After drying, 5 gram samples were kept at room temperature and subsequently used for ascorbic acid determination. Samples were, in addition, oven dried at 50°C overnight (16h), parceled into 5 g portions and kept at room temperature for 288 hours. Three sub-samples were withdrawn from the freezer or storage at room temperature for analysis.

Analytical Procedure

Proximate Composition: (crude protein, ether extract, crude fiber, ash, moisture and carbohydrate) was determined by the method of the Association of Official Analytical Chemists (AOAC, 1984).

Ascorbic acid: Was extracted from 5 g fresh samples or its equivalent with 0.1 % oxalic acid using a Kenwood KW10 food blender and determined as described earlier (Falade *et al.*, 2003).

Tannin: Was quantified by the modified Vanillin-Hydrochloric acid method (Price *et al.*, 1978).

Total oxalate: Content was determined by the method of Oke (1966) with slight modifications. 4.0 g of each sample was weighed in quadruplicate into conical flasks and extracted with a mixture of 190 mL distilled water and 10 mL 6 M HCl. The suspension was placed in a boiling water bath for 2 hours and filtered and made up to 250 mL with water in a volumetric flask. To 50 mL aliquot was added 10 mL 6 M HCl and filtered and the precipitate washed with hot water. The filtrate and the wash water were combined and titrated against conc. NH_4OH until the salmon pink colour of the methyl red indicator changed to faint yellow. The solution was heated to 90°C and 10 mL 5 % (w/v) $CaCl_2$ solution was added to precipitate the oxalate overnight. The precipitate was washed free of calcium with distilled water and then washed into 100 mL conical flask with 10 mL hot 25 % (v/v) H_2SO_4 and then with 15 mL distilled water. The final solution was heated to 90°C and titrated against a standard 0.05M $KMnO_4$ until a faint purple colour of the solution persisted for 30 s. The oxalate was then calculated as the sodium oxalate equivalent.

Statistical Analysis: The results were expressed as mean and standard deviation of three determinations. Statistically significant differences were determined by Duncan's Multiple Range Test (Zar, 1984).

Results and Discussion

The range of moisture content reported in Table 1 encompasses the 85-87 % moisture content reported earlier by Bradbury and Hammer (1988). The moisture content now reported for Amaranthus vegetable compare favourably with 87 % moisture content obtained earlier in our laboratory (Awoyinka *et al.*, 1995). There is no significant difference in the moisture content of the two varieties of both *Amaranthus viridis* and *Celosia argentea*. Crude protein ranged from 21 to 30 % in agreement with the lower values reported by Lucas (1988). The crude protein (CP) content of *Amaranthus viridis* now reported (Table 1) agreed favourably with the 26 % CP reported by Oyenuga (1968); higher than the 19.5 % reported for a similar sample from this laboratory but lower than the 30-33 % reported by Rangarajan *et al.*, (1998). The CP value reported for *C. argentea* (green variety) in this study was similar to 28 % reported for a similar sample by Lucas (1988) though the CP value for *C. olitorius* was slightly lower. Crude protein content of leafy vegetables vary with age; the young leaves of cassava for instance contained as much as 40 % crude protein while the mature leaves contained a paltry 22 % on dry matter basis (Ravindran, 1993). There was no significant difference in the crude protein content of the two varieties of *Amaranthus viridis* while a statistically significant difference (P> 0.05) was observed in the crude protein content of the two varieties of *Celosia argentea*. The difference in the crude protein of the two varieties of *C. argentea* is substantial enough to warrant a more detailed investigation of varieties planted at the same time to confirm the difference. The crude fiber content of the vegetables (Table 1) ranged from 3.2 to 9.7 %. The values reported for the two varieties of Amaranthus species agreed favourably with the 8.8-9.2% reported earlier (Lucas, 1988; Oyenuga, 1968). Crude fiber was higher (though not statistically) in the local variety of *Amaranthus viridis* than the introduced variety. The crude fiber content of the two varieties of *Celosia argentea* differed significantly with the crude fiber of the purple variety being closer to the 10.8 % crude fiber reported by FAO (1968) and slightly higher than the 7.2 % reported by Lucas (1988). The crude fiber content of the green variety of *C. argentea* was about 60 % that of the purple variety. Crude fiber increases with maturity (Oyenuga and Fetuga, 1975) therefore it may be necessary to investigate the differences further. Ether extract of the vegetables (Table 1) ranged between 3 and 14 %. The ether extract here reported for the green variety of *Amaranthus* species agreed well with the 3 % crude fat reported earlier by Lucas (1988) but higher than the 1.3 % published by FAO (1968). The ether extract of *Solanum* vegetable (5.3 %) compared well with 4.6 % reported by Oke in 1966 and 4.4 % by Lucas (1988) for a *Solanum* species while the ether extract of *C. olitorius* in the present study was within the 0-8 % range reported by FAO (1968). The ether extract of the local variety of *Amaranthus* was significantly higher than the exotic green variety being at least twice as much (Table 1) which again may be indicative of better nutrient composition in the local compared to the exotic variety. The ash content of the vegetables ranged between 5 and 13 % (Table 1) which

Table 1: The proximate composition and ascorbic acid content of some vegetables

Sample	%Moisture content	Crude Protein	Crude Fibre	Lipid	Ash	CHO	Ascorbic Acid mg/100g
		% dry weight					
Amaranthus viridis	86±0.4	26±0.4	7.9±0.2	3.1±0.5	11.7±0.8	52±2.3	386±11.4
Amaranthus viridis (Local variety)	86±0.5	27±0.3	9.0±0.2	7.1±1.7	13.0±0.3	44±2.9	468±21.2
Celosia argentea (Green variety)	89±1.0	26±0.3	4.8±0.4	4.5±0.3	12.2±0.4	52±5.1	450 ±20
Celosia argentea (Purple variety)	89±0.5	21±0.4	8.5±0.1	5.1±0.4	8.8±0.1	57±2.7	380 ±29
Cochorus olitorius	87±0.9	21±0.4	3.9±0.6	6.8±0.1	9.0±0.2	59 ±4.0	412±16
Solanum macrocarpon	84±1.7	23±0.2	9.7±0.2	5.3±0.1	6±1.9	56 ±3.2	256±6.6
Struchium spargonophora	91±0.1	30±0.6	3.2±0.7	7.6±1.9	11±1.0	48 ±2.5	70.4±4.2 (2.7±0.4)
Telfaria occidentalis	79±0.3	28±0.4	8.7±0.2	12.2±1.6	5.0±0.3	46 ±1.9	Nd
Vernonia amygdalina	87±0.4	24±03	8.8±0.2	14.3±0.6	7.6±0.3	45±2.2	109 ±3.7 (4.6±0.6)

[1]Mean ± standard deviation of triplicate analysis
Values in parenthesis are obtained from macerated samples

Table 2: Tannin and oxalate content of some nigerian vegetables on dry weight basis[1]

Sample	Tannin (mg g^{-1})	Total Oxalate (g/100 g)
Amaranthus viridis	3.0±0.1	8.7±0.8
Amaranthus viridis (Local variety)	3.5±0.0	9.3±0.2
Celosia argentea (Green variety)	4.1±0.6	16.9±0.6
Celosia argentea (Purple variety)	4.6±0.4	17.8±1.4
Cochorus olitorius	Nd	Nd
Solanum macrocarpon	Nd	Nd
Struchium spargonophora	1.4±0.6 (1.6±0.4)	2.4±0.3 (2.2±0.9)
Vernonia amygdalina	1.7±0.9 (1.7±0.9)	2.4±0.0 (3.0±0.0)

[1]Mean ± standard deviation of quadruplicate analysis.
Values in parenthesis are obtained from macerated samples.

Table 3: The effect of processing on the ascorbic acid content of two nigerian vegetables (mg / 100 g dry weight)

Duration of Processing/ Storage	*Processed Amaranthus caudatus*				*Processed Struchium spargonophoraHour*			
	Fresh	Blanched	Oven dried	Sun dried	Fresh	Blanched	Oven dried	Sun dried
0	482±3.6	419±3.1	482±3.6	482±3.6	71.8±2.5	63.0±0.6	71.8 ±2.5	71.8±2.5
48	484±9.5	379±7.4	14.0±1.0	10.6±1.9	62.5±4.1	55.8±3.7	8.1±0.6	9.2±1.0
96	487±10.9	352±7.9	7.0±0.9	8.5±0.0	50.2±7.0	52.7±6.7	5.0±0.3	5.2±0.0
192	339±21.3	338±21	5.0±0.9	5.3±0.8	50.4±0.9	33.3±0.6	6.4±0.0	2.6±0.0
288	351±2.1	137±0.8	4.0±0.0	4.2±0.0	50.6±1.7	33.3±1.1	2.5±0.1	2.6±0.1

were in the lower 50 % of the 6-26 % range reported by FAO (1968). The ash content of *C. olitorius* fell within the 6-19 % range reported for the various types of the same vegetable (FAO, 1968). The ash content of a plant food source varies with location and soil type but there was no significant difference in the ash content of the two varieties of *Amaranthus* species under investigation while the difference in that of the two varieties of *C. argentea* was statistically significant. Carbohydrate content as expected was lower in the local variety of *Amaranthus viridis* compared to its exotic green variety as a result of the higher nutrient content in the former (Table 1) while the difference in the carbohydrate content of the two varieties of *C. argentea* was not statistically significant.

Ascorbic acid is an important water soluble vitamin already implicated in most of the life processes but principally functions as an antioxidant. It is present abundantly in fruits and vegetables where the common man in the developing countries receives most of their daily intake. The level of this vitamin in vegetables which supply about 88 % of the protein need in the tropic and the effect of processing techniques on its availability become very important. The ascorbic acid content of the vegetables ranged from 70 to 468 mg / 100 g dry weight for *S. spargonophora* and the local variety of *Amaranthus* vegetable respectively (Table 1). The ascorbic acid content of

these vegetables (except *S. spargonophora*) was higher than that of lettuce, spinach, green pepper, green onions and tomatoes (Zennie and Ogzewalla, 1977) and the values were within the range reported by Achinewhu (1983). The value now reported as the ascorbic acid content of *C. olitorius* was within the range of 45-100 mg / 100 g wet weight reported earlier (FAO, 1968) for this vegetable. The ascorbic acid content of the local variety of Amaranthus agreed favourably with the 68 mg / 100 g reported by Oyenuga (1968) and 64 mg / 100 g by FAO (1968) on wet weight basis for Amaranthus vegetable while the ascorbic acid content of the both varieties of Amaranthus were also within the range of 50-90 mg / 100 g wet weight for spinach (Machlin, 1991).
The green *C. argentea* vegetable has a statistically higher content of crude protein, ash and less of crude fibre and total carbohydrate compared to the purple variety. In addition, the ascorbic acid content of the green variety is 16 % higher than that of the purple even though both varieties contain a similar level of moisture and are therefore expected to be succulent to the same degree. The higher level of essential nutrients in the green variety of the *C. argentea* coupled with its lower level of antinutritional factors such as tannin and oxalate (Table 2) could justify the introduction of the exotic green variety of *C. argentea* but could the same argument hold for Amaranthus varieties? The local variety of *A. viridis* contained a slightly higher crude protein, ash and crude fibre content and a statistically higher level of ascorbic acid and lipid content compared to the exotic green variety (Table 1). This therefore could not be the basis of introducing the exotic variety. Oke (1966) reported the oxalate content of *Amaranthus caudatus* to be as much as 11.5 % and called for a breeding program to reduce this almost toxic level of oxalate in some vegetables in view of the fact that most Nigerians depend on vegetables for their supply of crude protein, mineral and vitamins. The oxalate content of the exotic variety is about 10 % lower than the local variety while the tannin content is also not appreciably different. If the introduction of the exotic variety of A. amaranthus is based on the oxalate level then it can be assumed that the breeding program has not succeeded since the oxalate content of both local and exotic varieties of Amaranthus still contained an appreciable level of oxalate ranging between 75 and 80 % of the value reported by Oke in 1966. Except there are other nutritional factors such as vitamins not considered in this study, it would be safe to conclude that the local variety of *A. caudatus* is nutritionally better than its exotic variety.
The Recommended Daily Allowance (RDA) for ascorbic acid is 60 mg (FNB, 1969) for an average man or woman during pregnancy or lactation and this quantity can be provided by 200 g of each vegetable if it is stable during processing.

The Effect of Processing on Ascorbic Acid and some Antinutritional Factors: Methods of processing vegetables for culinary purposes differ from one community to the other but some processes are now common to most tribes in Nigeria. Blanching in hot water for at least 10 minutes is a standard method of processing vegetables for consumption. This processing method reduced the ascorbic acid content of the representative vegetables – *Amaranthus* and *Struchium* by 12-13 % (Table 3) in agreement with the earlier observation of Howard *et al.* (1999). *Vernonia amygdalina* and *Struchium spargonophora* are bitter to taste and in many communities, these vegetables are macerated in water, at times with salt added, squeezed and the solid material used as the potherb while the liquid part is discarded. This procedure effectively extracts most of the ascorbic acid content into the liquor such that the leafy vegetable contained 3.8-4.5 % of the original ascorbic acid content (Table 1). Unfortunately, the liquor is discarded and with it virtually all the ascorbic acid content and probably some or most of the other water soluble vitamins. In addition, the tannin content of the vegetables marginally increased as in the case of *Struchium* (14 %) or remained constant as in *Vernonia* (Table 2). The oxalate level remained fairly constant in *Struchium* with a mere 8 % reduction from the original level but increased by 25 % in Vernonia (Table 2).

Effect of Processing and Storage: Vegetables are usually not stored for a long period of time in Nigeria with the notable exception of Okra (*Hibiscus esculentus* L.) which is dried before storage. However, there have been some attempts to preserve some of the Nigerian local vegetables to bridge the scarcity in the dry harmattan months of December to March. Sun drying is a major processing method in rural environment and the products are kept at room temperature until needed. This study mimicked this condition and compared the result with that obtained from the oven drying method. All the storage techniques in this study led to a loss in the ascorbic acid content of the samples though to varying degrees. This is consistent with the observation of Mathooko and Kiniiya (2002) of a gradual loss in ascorbic acid content during storage which could not be completely prevented by the application of sodium metabisulfite as a preservative. There was no change in the ascorbic acid content of the fresh Amaranthus during the first 96 h of storage, a 30 % decrease during the next 96 h and was stable in the last 96 h of storage. There was a 27 % decrease in the total ascorbic acid content over the 288 h storage period similar to the 21 % loss of ascorbic acid when herbal tea was freeze dried (Mohanom *et al.*, 1999). In the blanched Amaranthus sample, there was a gradual decrease in the ascorbic acid in the first 192 h amounting to less than 20 % of the total ascorbic acid content while there was a 59 % reduction in the last 96 h so that there was an aggregate loss of 67 % of its original ascorbic acid content during the 288 h storage period. Fresh *Struchium* vegetable sample also lost 27 % of the total ascorbic acid content after 12 days (288 h) of storage in the freezer. In this sample there was also a gradual loss of 30 % of the ascorbic acid content in the first 96 h and thereafter remained stable (Table 3). Ascorbic acid in the blanched *Struchium* vegetable sample decreased gradually in the first 96 h, drastically (37 %) in the next 96 h and thereafter remained stable till the end of the storage period. There was a total of 47 % loss in the ascorbic acid content during the 288 h storage period of this blanched sample. The result reported here is not surprising since a stable or even marginal increase in the ascorbic acid content of vegetables has been reported after initial reductions (Benkeblia and Khali 1996). The sun and oven dried materials lost all their ascorbic acid content (about 99 %) during the storage period at room temperature as presented in Table 3. Indeed, both sun and oven drying methods resulted in about 97 - 98 % loss in ascorbic acid in *Amaranthus* and 87-89 % in *Struchium* samples after the first 48 h. A decrease of 76 % in the ascorbic acid content was reported by Mohanom *et al.*, (1999) when herbal tea was dried at 50°C for 9 h but that this loss was reduced to 34 % when the drying temperature was raised to70°C and the duration was reduced to 5 h. Howard *et al.* (1999) reported a loss of over 90 % of the ascorbic acid content of some vegetables refrigerated for 16 days and a linear decrease in frozen vegetable samples. Benkeblia and Khali (1996) also reported a decrease in the ascorbic acid content of onions stored at 4°C while Achinewhu (1983) also reported that traditional processing of vegetables resulted in a 32 – 68 % loss of ascorbic acid and that exposure to the environment at 27°C for 4 h led to a loss of ascorbic acid between 22 and 34 %.

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