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Effects of Hot Smoking and Sun Drying Processes on Nutritional Composition of Giant Tiger Shrimp (*Penaeus monodon*, Fabricius, 1798)

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There are information gaps in the knowledge of the impacts of traditional techniques of fish preservation used to meet market demands even though there are growing concerns of the effects of these methods of preservation on product forms and qualities. In this study the effects of commonly used preservation techniques of hot smoking and sun-drying on the nutritional composition of *Penaeus monodon* were investigated. Proximate values varied significantly (P<0.05) except for protein the dominant constituent with an average value of 64%. Stearic acid varied significantly (P<0.05) with lowest values of 2.30% in smoked specimens. Oleic acid was the highest fatty acid thus the predominance of the monounsaturated fatty acids (MUFA) with smoked samples having predominant (P<0.05) values. ω -3/ ω -6 ratios of 7.76, 13.01 and 8.16 in fresh, smoked and sundried were in favour of the omega 3 with EPA (16.95±0.76-18.43±1.01%) being significantly higher (P<0.05) to the DHA (9.36±0.54-11.90±0.27%). Smoked forms had significantly higher values (P<0.05) of alanine, threonine, tyrosine and cysteine. Arginine and histidine were significantly raised (P<0.05) in sundried specimens. Isoleucine, methionine, aspartate, glycine and proline remained highest (P<0.05) in fresh samples. Lysine was limiting in smoked and sundried specimens. Smoked products offered healthiest advantage with the lowest values of saturated fatty acids (25.10%), index of atherogenicity (0.58), index of thrombogenicity (0.20) and bearing in mind goal of reduced coronary heart disease (CHD) in food consumption. This paper offers the first holistic work on nutritional evaluations of the three commonest forms for which Giant tiger shrimps are frequently consumed.

INTRODUCTION

In Nigeria and West Africa generally, about 80% of the fish is consumed smoked and the remaining as fresh, salted, sundried or fried [FAO, 2008]. Ward [2003] estimated the quantity of smoked fish from West Africa entering the United Kingdom to be in the region of 500 tonnes per year with a retail value of £5.8 to £9.35 million. Smoking is one of the most ancient processing and preservation technologies which have been for centuries. The preservative effect is generally attributed to the anti-oxidant and anti-microbial properties of phenolic compounds.

Smoking technology is of two forms, hot and cold smoking. Cold smoking is achieved without thermal treatment usually at temperature below 30°C whereas; the commonly used method of hot smoking is carried out at thermal temperature of 70-80°C [Bykowski & Dutkiewicz, 1996] using the traditional kiln with wood burning temperature of between 300 and 700°C usually above the 80°C of the oven's temperature [Nti et al., 2002]. Three processes cooking, drying and smoking are involved in hot smoking resulting in a longer product

* Corresponding Author: E-mail: shehu.akintola@lasunigeria.org (S.L. Akintola) shelf life of 6-9 months when stored properly [UNDP, 2001] and able to keep in check some bacteria. However, there are growing concerns on the wood smoke and inability to control smoking temperature in the traditional kiln resulting in release of toxic substances such as PAHs and phenols [Essumang *et al.*, 2013].

Similarly sun drying has found favour with fish mongers for centuries and produced fish meat that is condensed, saturated with oil, translucent and acquired an amber colour, a typical flavour, dense consistency and pleasant taste [Gerasin & Antonova, 1979]. Limitations of this method include considerable product losses, lower fish quality because of contamination by foreign materials, insects and microorganisms as well as discolouring by ultraviolet radiation [Tiwari & Sarkar, 2007].

Penaeus monodon has adequate proximate compositions that meet dietary needs of human. Marichamy et al. [2011] reported that 20.34% protein in P. monodon was highest of the eight species of fin and shell fish studied. Shrimp meat is an excellent source of protein [Yanar & Celik, 2006; Sriket et al., 2007]. According to Chen et al. [2007] essential amino acid composition is one of the most important nutritional qualities of protein while amino acid quality may be assessed using the amino acid score. Nutritional quality of fish is to a great extent associated with the content of essential fatty acids.

Nevertheless, cooking and preservation techniques could cause modifications in proximate composition, fatty acids and amino acids as well as changes in solubility and nutritional quality of fish [Castrillon *et al.*, 1997; Yamamoto & Imose, 1989; Selmi *et al.*, 2010]. It is obvious that smoking and sun drying are able to meet the market objectives for which the methods have been commonly used by fish mongers and artisanal fishers globally particularly in West Africa.

Also, ground crayfish (local and markets names for shrimp, prawns and crayfish) are increasingly being used as ingredients to weaning/complementary foods in many developing countries such as gruel (pap or porridge), moi-moi (black eye beans-cowpea), ogi/ugi (fermented corn, millets, and guinea corn) - in Western Nigeria/Eastern Africa. This practice is based on advice of health workers' goals of improved palatability and reduced malnutrition to vast number of the poor who are not able to afford the formulated diets. There has not been any study to evaluate the impact of such intervention on the child nutrition [Ehiri et al., 2001] and starting point for such query will be providing information on the nutritional status of the ingredients.

Concerns of nutritional loss on account of preservation techniques are therefore justified. However there are obvious gaps in information supply on the effects of traditional methods of hot smoking and sun drying processes on the proximate composition, amino acids and fatty acids composition of the end products of these widely use methods in preservation of aquatic products such as the *Penaeus monodon*. In the same vein, the nutritional qualities of the products emanating from using these techniques have been poorly understood.

Our study elucidated on the missing information required for objective analyses of the impact of traditional preservatives techniques on an important dietary ingredient, *P. monodon*. To the best of our knowledge it is the first attempt to describe in details dietary factors of the shrimp products across fresh, smoked and sundried forms they are frequently consumed against the high incidence and concerns of diet based diseases. This is an important addition to literature on food and nutritional studies of data poor informal sector of the food industry.

This study provided information on the impact of hot smoking and sun drying on the shrimp with further information on the extent to which fresh, smoked and sundried products are able to meet dietary amino acid requirement of consumers of these products. It evaluated and compared the impact of smoking and sun-drying processes on the proximate, fatty and amino acids compositions of the giant tiger shrimp which intake have been reported to promote the well-being of humans.

MATERIALS AND METHODS

Sample collection and processing

Penaeus monodon weighing 64.46-301.21 g were collected in February 2011 from shrimp trawlers (Karflex Jetty Kirikiri Town, Apapa, Lagos) with otter-trawl net (15 mm mesh size at the sides and 12 mm at its end). The trawlers fishing ground was FAO zone 34,100 nautical miles of the Nigerian coast. Shrimp samples collected were iced (shrimp and ice at

the rate of 1:1) immediately in a plastic ice box and transported within 30 min to Nigerian Institute for Oceanography and Marine Research (NIOMR) Lagos for processing in the laboratory.

The shrimps were washed, blotted dried and weighed. Afterwards, heads, shells, tails, legs and intestines were removed and weights of the samples were takeng using the weighing balance. Afterward, specimens (n=45) within the same weight range (mean=150 \pm 0.25 g) and total length (mean=85 \pm 0.15 mm) were separated to three clusters from each of the three sample lots in each independent experiment available for this study: (i) fresh samples were stored at -40°C for 2 h and used as control, (ii) subjected to smoking, and (iii) subjected to sun drying.

Smoking

The smoking treatment adopted was the "hot smoke drying". Shrimps were laid out on a platform of wire mesh supported by a semi-circular frame work of perforated metal drum measuring 0.846 m² for 2-3 h process of smoking with uniform smoking ensured by using feather objects to turn the shrimps until uniform brownish colour was observed. The base of the drum was filled with sharp sand up to 10 inches. Six fire wood sticks (*Khaya ivorensis*) of average length of 0.6 m and thickness of 0.05 m, firewood chips were used to make fire that was allowed to heat up for about 15 min. An average temperature of 160°F (71°C) was recorded during smoking with mercury in a glass thermometer.

Sun drying

The shrimps were placed in a circular clean aluminium tray that was covered with a mosquito net to prevent access by flies and other insect. Samples were sun dried from 8am to 4pm at an average ambient temperature of 31°C. The average internal temperature of the tray was 30°C. The tray was always kept indoors after 4pm in a room with an average ambient temperature of about 29°C for two days. Shrimps were turned over every three hours and on the third day sundried from 10am to 1pm after which they were taken to the laboratory.

Proximate composition

The proximate compositions were determined following the AOAC [2006] methods. The moisture content was determined by method no 934.01, protein and ash contents were done according to methods 984.13 and 942.05. Both fat and fiber were according to method 920.39 (A). Carbohydrate was calculated by difference.

Chemical analyses

Analyses of fatty acid

Oil extraction

The fat of the grinded sample from the control (fresh) and experimental (smoked and sundry) material was extracted with redistilled *n*-hexane for the recovery of the undiluted oil using Soxhlet arrangement. The crude oil extract was made to be free of filtering through the anhydrous sodium sulphate salt. The hexane was removed from the oil/hexane mixture by using rotatory evaporator at 71°C under atmospheric pressure.

Fatty acid methyl ester analysis

Fatty acid profile - saturated, mono-and polyunsaturated analyses were carried out by the following modified AOAC [1990] and AOAC [2005] official methods. The fatty acid methyl esters were analysed using HP 6890 powered with HP Chem Station Rev. A 09.01 (1206) Software equipped with an HP INNOWax capillary column, (30 m x 0.25 mm x 0.25 μ m). Nitrogen was used as the gas carrier and furnace temperature was 60°C. The injection temperature was 250°C with a split ratio of 20:1. The flame-ionization detector (FID) temperature was held at 320°C.

Fatty acid identification

The fatty acids methyl esters were identified by comparing the retention time of the samples against C19:0 (10 mg/L concentration) that was used as fatty acids esters internal standard. The relative percentage of the area was obtained by using the following equation: Area % $FA_x = (A_x/A_R) \times 100$, where: $FA_x = fatty$ acid to be identified, $A_x = a$ area of the methyl esters X and $A_R = t$ total area of the chromatogram. Peak areas lower than 0.1% of total area were not considered.

Indices of lipid quality

Indices of atherogenicity (IA) and thrombogenicity were determined following Ulbricht & Southgate [1991]:

IA= $((12:0 + (4X14:0) + 16:0)/[\Sigma MUFAs + \Sigma PUFA-n6 + \Sigma PUFA-n3)$

IT= $((14:0 + 16:0) + 18:0)/((0.5 \text{ X} \Sigma \text{MUFAs} + 0.5 \text{ X})$ PUFA-n6+3 X $\Sigma \text{PUFA-n3} + [\Sigma \text{PUFA-n3}/\Sigma \text{PUFA-n6}))$

Analysis of amino acids

Amino acid extraction was achieved by modified AOAC method [2006]. It is noteworthy that tryptophan was not determined with this hydrolysis procedure. Dried and pulverized samples were made to be free of water, defatted with 30 mL of the petroleum spirit using Soxhlet equipped with thimble and extract hydrolysed using 6 mol/L of hydrochloric acid (HCl) at 110°C for a day. The amino acid content of the sample was recovered by extraction with 30 mL of the methylene chloride and concentrated to 1 mL for gas chromatography analysis. Gas chromatography was carried out using HP 6890 powered with HP ChemStation Rev. A 09.01 (1206) software and the capillary column HP 5 (30 m x 0.25 mm x 0.25 μ m). Hydrogen was used as the gas carrier with furnace temperature at 60°C. Injection temperature was 250°C with a split ratio of 20:1. Oven programs were carried out with Pulsed Flame Photometry Detector (PFPD) at 320°C. The results were expressed as g of AA per 100 g Black tiger shrimp flesh.

Amino acid score

Essential amino acid scores in the treatments were calculated with respect to the FAO/WHO reference amino acid pattern of the preschool child (2–5 year) [FAO/WHO/UNU, 1985].

Amino acid score= Sample amino acid/Reference amino acid \times 100

Protein Digestibility Corrected Amino Acids Score (PDCAAS)

The PDCAAS was calculated for each product form by multiplying the lowest uncorrected amino acid score by the food protein's digestibility [FAO, 1991]:

 $AAS \times true digestibility.$

Statistical analyses

All of the extraction and composition analyses were conducted in triplicates from three independent experiments conducted for the study. Results were expressed as mean values \pm standard deviation (SD). The differences between the mean values of *Penaeus monodon* meat in fresh, smoked and sundried samples were calculated using one-way analysis of variance (ANOVA), and statistically significant differences were reported at P<0.05. The Least Significant Difference (LSD) was conducted for independent sample t test as may be required between two treatments. Data analyses were done with the use of SPSS 15.0 software.

RESULTS AND DISCUSSION

Proximate composition

Changes in the proximate composition of fresh, smoked and sundried *Penaeus monodon* are shown in Table 1. The mean moisture content for fresh *P. monodon* was 75.18±0.32% and was comparable to those reported for shell fishes such as *Metapenaeus affinis, Anadara granosa* and *Ostrea spp* [Nurnadia *et al.*, 2011]. Higher values of 78.66% and 82.21% (wet weight) were reported for shrimps such as *Parapenaeus longirostris* and *Plesionika martia* [Oksuz *et al.*, 2009]. During smoking and sun drying processes approximately one-quarters and one-thirds of moisture were last, which meant that both processes were responsible for the lower moisture values in the products.

Protein mean values (64.74-64.20%) observed were comparable to values (dry weight) reported in muscle of Penaeus monodon (63.22%), Metapenaeus monoceros (60.15%) and Macrobrachium scariculum (56.75%) [Snehalata & Sahu, 2001; Dinakaran et al., 2010]. Based on dry weight, protein was the dominant biochemical constituent, an observation similar to that of Achuthankutyy & Perelekar [1984] in the fresh and the two processing methods investigated. In this study protein values were not significantly different (P>0.05) between fresh and the two drying processes and this observation was due to the removal of moisture arising from the dry weight basis for which evaluation was carried out. Much lower values of protein (wet weight) have been reported in Indian white shrimp (41.3%), cuttlefish (13.94%), prawn (19.12%), cockles (15.99%) and oyster (13.31%) [Ravichandran et al., 2009; Nurnadia et al., 2011]. Dry weight sample preparation apparently accounted for higher protein values obtained in the three product forms in this study.

Sundried specimen showed the highest proportion of crude fat (5.84%) found to differ significantly (P<0.05) between the control and the two drying processes. These findings are in accordance with those of Snehalata & Sahu [2001] who reported 5.94% of crude fat in muscle of *Penaeus monodon* (dry weight). Increased levels of crude fat in both

TABLE 1. Proximate composition	(% on a dry weight basis) of Pengeus monodon sub	iected to smoking and su	indrying processes
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Proximate characteristics (%)	Fresh	Smoked	Sundried
Moisture	(75.18±0.32)	(54.52±0.72)	(50.47 ± 0.72)
Protein	64.74±0.45	64.27 ± 0.06	64.20 ± 0.03
Lipids	$4.88 \pm 0.04^{a,b}$	$5.69 \pm 0.06^{a,c}$	$5.84 \pm 0.11^{\text{b,c}}$
Ash	$12.66 \pm 0.17^{a,b}$	13.35 ± 0.39^a	13.57 ± 0.10^{b}
Fibre	$14.48 \pm 0.41^{a,b}$	$13.26 \pm 0.26^{a,c}$	12.06±0.23 ^{b,c}
Carbohydrate	3.24 ± 0.20^{b}	3.44±0.13°	4.35±0.14 ^{b, c}

Values are given as means \pm SD from triplicate determinations of three independent experiments. ^a values are significantly different (p<0.05) between fresh and smoked samples by the Independent-Sample *t* test from LSD. ^b values are significantly different (p<0.05) between fresh and sun dried samples by the Independent-Sample *t* test from LSD. ^c values are significantly different (p<0.05) between smoked and sun dried samples by the Independent-Sample *t* test.

controls may be adduced to moisture loss. In our data moisture content loss in the final smoked and sundried products (54.52% and 50.47%, respectively) lessen approximately one-half times compared with the initial product (75.18%).

Ash contents in sundried (13.57%) and smoked (13.35%) forms were higher compared to the value obtained in the fresh material (12.66%). The processes of smoking and sun-drying significantly increased (P < 0.05) the ash contents of the shrimp and could be related to moisture loss induced by both processing methods. This finding is similar to those of Selmi *et al.* [2010] who reported increased ash contents in fresh silverside (1.96%) during solar (6.21%) and experimental drying process (5.13%) on the account of water evaporation.

Fiber content in fresh black tiger prawn in our study was 14.48% and was similar to 16.67% reported by Roostita *et al.* [2010] for the same shrimp's processing waste (skin, head and tail). However, these values were higher than that found in the flesh (8.2%) and shell (8.7%) of fresh *Penaeus indicus* (dry weight) [Ravichandran *et al.*, 2009] but approximate to the values reported by Adeyeye *et al.* [2008] for flesh (8.9%) and shell (9.6%) of *Penaeus notabilis*. Both processing methods significantly (P<0.05) reduced the fiber contents in the muscle of the shrimp and which therefore can be explained by the impact of heat generated by the processing methods. The difference between the higher values obtained for the fibers in *P. monodon* and other crustaceans may be species related.

The carbohydrate average value of 3.68% for all the product forms was comparable to the value in muscle (dry weight) of *Penaeus monodon* (5.08%) [Snehalata & Sahu, 2001]. Carbohydrate contents were the lowest components in the fresh and dried forms of the shrimp investigated. Our study is similar and agreed with the deduction of Sree *et al.* [1994] which stated that low carbohydrate in marine animals was due to the fact that glycogen does not contribute much to reserves in their body.

Asymmetrical relationship observed wherein smoking and sun-drying lowered significantly (P<0.05) the fiber content while the carbohydrate value in both processing methods were significantly higher (P<0.05) shows the impact of the two heating processes on the structure of the shrimp. We proposed, as deduced from our results, that during heating the crude fiber

constituting the cell wall was reduced while the carbohydrate components were increased relative to the values obtained in the fresh samples. To our knowledge there is no information on the impact of any heat treatment on the structural composition of the shrimp's carbohydrate and in the light of our finding this opens up the need for investigation of the relationship between heat treatments and carbohydrate composition of the shrimp. The fresh samples will offer higher dietary fiber with advantage of being helpful in promoting digestion and lowering occurrence of constipation.

Non-polar fatty acids concentration

The non-polar lipid fatty acid composition of *Penaeus monodon* based on respective methods of preservation evaluated is shown in Table 2. Values of the monounsaturated fatty acids (MUFA) constituted the majority of the fatty acids (highest value in smoked form; 44.97%) followed by the polyunsaturated fatty acids (PUFA; fresh being the highest; 33.07%) and saturated fatty acids (SFA; lowest value of 22.8% in smoked). The PUFAs were reported to be the predominant total lipid fatty acids in the meat of *P. monodon* (44.4%), and the seven shrimps investigated (32.8-47.5%) [Sriket *et al.*, 2007; Li *et al.*, 2011]. In the adult and juvenile individuals of *Chirocephalus kerkyrensis* and *Litopenaeus vannamei* respectively SFAs were the dominant [Mura *et al.*, 2007; Zhou *et al.*, 2007].

Short Chain (saturated) Fatty Acids (SCFA) - acetic (2:0), propionic (3:0), and butyric (4:0) - were not observed in Penaeus monodon similarly to studies of Chedoloh et al. [2011]. This trend is a general pattern in crustaceans in view of the works of Chedoloh et al. [2011] and Tsape et al. [2010]. Capric acid (10:0) was the only medium chain SFA observed with highest mean values of 0.72% in the fresh sample (Table 2) and this was the first to be reported as gleaned from literature. The presence of capric acid in the shrimp obtained in this study may be due to geographical differences compared to other works from other countries with no report of capric acid. Budge et al. [2002] reported within species variation in fatty acid composition due to geographical differences. Tissues of *Penaeus monodon* were dominated by the presence of long chain SFA, C12:0-C18:0. Long chain SFA, C19:0-C24:0 total lipid have been reported in the muscle and cepha-

TABLE 2. Fatty acid profile of raw, smoked and sundried muscle of *Penaeus monodon* (%).

Fatty acids	Fresh	Smoked	Sundried
Saturated	fatty acids (SFA)		
C 10:0 Capric Decanoic	0.75±0.02	0.33 ± 0.30	0.40±0.22
C 12:0 Lauric Dodecanoic	0.62 ± 0.08	0.28 ± 0.25	0.38 ± 0.20
C 14:0 Myristic Tetradecanoic	7.69 ± 1.22	7.08 ± 0.54	8.32 ± 0.17
C 16:0 Palmitic Hexadecanoic	16.49 ± 0.06	15.11 ± 0.68	16.88 ± 1.35
C 18:0 Stearic Octadecanoic	$3.09 \pm 0.02^{a,b}$	2.30±0.20 ^{a,b,d}	$3.25 \pm 0.06^{a,d}$
Σ SFA	28. 64	25.10	29.23
Monounsaturat	ed fatty acids (MUFA)		
C16:1 n-7 Palmitoleic cis-9-hexadecenoic	11.66±0.17	12.48±1.07	11.54±0.37
C18:1 n-9 Oleic cis-9-Octadecenoic	$22.31 \pm 0.62^{a,b,c}$	$27.11 \pm 2.00^{a,b,d}$	$24.72 \pm 0.95^{a,c,d}$
C22:1 n-9 Erucic cis-13-Docosenoic	4.32±0.03	5.38 ± 0.78^{d}	4.47 ± 0.08^d
∑ MUFA	38.29	44.97	40.73
Polyunsaturate	ed fatty acids (PUFA)		
C18:2 n-6 Linoleic 9-12,octadecadienoic	1.77±0.11 ^{a,b}	0.86±0.22 ^{a,b,d}	1.57±0.24 ^{a,d}
C18:3 n-6 gamma Linolenic cis-6,9,12-Octadecatrienoic	0.89 ± 0.08	0.61 ± 0.19	0.76 ± 0.06
C20:4 n-6 Arachidonic cis-5,8,11,14-Eicosatetraenoic	$1.10 \pm 0.04^{a,b}$	$0.67 \pm 0.20^{a,b,d}$	$0.95 \pm 0.10^{a,d}$
C20:5 n-3 Eicosapentaenoic cis-5,8,11,14,17-Eicosapentanoic	17.41 ± 0.71	18.43 ± 1.01	16.95 ± 0.76
C22:6 n-3 Docosahexaenoic cis-4,7,10,13,16,19-Docosahexaenoic	11.90±0.27 ^{a,b,c}	9.36 ± 0.54 a,b	$9.81 \pm 0.53^{a,c}$
Σ PUFA	33.07	29.93	30.04
DHA/EPA	0.68	0.51	0.58
∑n-3 PUFA	29.11	27.84	26.76
Σn-6 PUFA	3.75	2.14	3.28
ω-3/ ω-6 IA IT	7.76 0.67 0.23	13.01 0.58 0.20	8.16 0.71 0.26

Values are given as means \pm SD from triplicate determinations of three independent experiments. ^a Values are significantly different (P<0.05) across the row subjected ANOVA. ^b values are significantly different (p<0.05) between raw and smoked samples by the paired *t* test from LSD. ^c values are significantly different (p<0.05) between raw and sun dried samples by the paired *t* test from LSD. ^d values are significantly different (p<0.05) between smoked and sun dried samples by the paired *t* test.

lothorax of *L. vannamei*, *P. monodon*, *M. rosenbergii* and *P. kerathurus* [Chedoloh *et al.*, 2011; Tsape *et al.*, 2010].

The highest concentration of SFA was observed in sundried form with concentration value of 29.24%. The value ranges of 25.4-28.46% for smoked and fresh treatments were lower compared to 43.8% reported for *P. monodon* in Southern Thailand by Chedoloh *et al.* [2011]. Smoked samples had the lowest value of SFA in this study suggesting a more intense oxidative degradation of the shrimps submitted to hot smoking than those found in fresh and sundried. Consumption of smoked product based on this study offers nutritional advantage to consumers since food product with lower SFA offers health benefit in light of the fact that food products with high levels of SFA have been linked to increased total and LDL-cholesterol levels and consequently coronary heart disease, CHD [Stanley, 2009].

The changes in SFA namely capric, lauric, myristic and palmitic acids (C10:0, C12:0, C14:0, and C16:0) were not significant (P>0.05) except for the stearic acid with 2.30% lowest value in the smoked specimen that is significantly different (P<0.05) in all forms. Even when a significant statistical variation of the stearic acid was found between the control and treatments, the difference in percentage of the fatty acid was small. Stearic acid is known to be a very stable saturated fatty acid [Žilić et al., 2010] and changes noticed may be accounted for by the high temperature of the hot smoking leading to an elevation of the MUFAs (particularly oleic acid), and may have resulted in the observed changes. In the same vein the biological peculiarities of the stearic acid from palmitic, myristic and lauric had been alluded to by Stanley [2009].

The most abundant SFA in this result was palmitic acid, in all the treatments. Palmitic acid (20.9%, 22.2%) was

the highest reported [Chedoloh et al., 2011; Sriket et al., 2007] for the black tiger shrimp thus our study lend weight with most studies for shrimps. The merit and demerit of individual component of long chain SFAs with regards to human health is confusing based on the view of Tvrzicka [2011]. Although, the value of capric acid rarely exceeded 2.5% of the total SFA in the control and treatments, consumption of the shrimp in whatever form is plausible taken into accounts the health benefit of the capric acid. Hainer et al. [1994] reported the role of medium chain SFA in the dietary treatment of obesity.

In the MUFAs, palmitoleic acid (C16:1 n-7) values did not change significantly (P>0.05) in the treatment and compared favourably with the concentration reported for curimbata (12.6%, 11.9%) but higher against that of seabob shrimp (4.74%, 4.55%) at summer and winter in Brazil [Luzia *et al.*, 2003]. Season, sun-drying and smoking may have little effect in shrimps. Both smoked and sundried specimens significantly (P<0.05) raised the value of erucic acid (C22:1 n-9) from the mean value of 4.52% in the fresh sample. Obviously the increased values were as results of the heat treatments adapted in our study and confirmed that erucic acid are raised when heat processing methods such as irradiation are applied to *Penaeus vannamei* (0.10-0.14% for 0-4 kGy doses) [Abreu *et al.*, 2010] and *Dicentrarchus labrax* (0.15-0.21% at 0-5 kGy doses) [Özden, & Erkan, 2010].

The predominant MUFA in all the treatments was the oleic acid an observation congruent to Li et al. [2011] and Sriket et al. [2007]. Values of oleic acid (C18:1 n-9) differed significantly (P<0.05) in all forms. The highest concentration of oleic acid was obtained in the smoked samples with mean value of 27.11%. The two preservation methods raised the value of oleic acid suggesting the positive influence by the two treatments as well as the nutritional advantages to consumers due to hypocholesterolemic effect of oleic acid. Similarly, oleic acid values were raised with increasing radiation dosages in headed shrimp (6.75-12.15%) [Abreu et al., 2010] and sea bream (20.19-20.25%) [Erkan & Özden, 2007]. Higher values reported in this study against 9.94%, 13.2%, and 10.7-15.8% [Sriket et al., 2007; Chedoloh et al., 2011; Li et al., 2011] for the same and other shrimp(s) may be on account of different shrimp sizes for the studies and geographical locations as well as environmental factors alluded to by Mura et al. [2000].

Values of gamma linolenic acid and eicosapentaenoic acid, EPA (C18:3 n-6 and C20:5 n-3) did not change significantly (P>0.05) between methods of preparations and implied that both methods do not have impact and their products are not easily subjected to oxidation. The values of gamma linolenic acid did not change in the fish subjected to different storage and cooking process by de Castro *et al.* [2007].

The preservation methods significantly (P<0.05) impacted on the proportion of C18:2 n-6 linoleic 9-12,octadecadienoic, C20:4 n-6 arachidonic, cis-5,8,11,14-eicosatetraenoic, C22:6 n-3 docosahexaenoic, and cis-4,7,10,13,16,19-docosahexaenoic acids. These changes were remarkable as fresh and smoked specimens values were lessen approximately by half while in sundried and fresh it was reduced approximately by a quarter. The high oxidation rate of docosahexaenoic, C22:6 n-3 reported by de Castro *et al.* [2007] was further confirmed in this study.

In the ω -3 series, the EPA was dominant over the DHA in all product forms. Content of EPA (C 20:5 n-3) being equal or greater than that of DHA (C 22:6 n-3) is a distinguishing feature of crustaceans and mollusks [Ackman, 2000]. The smoked specimens had highest concentration of 18.43% of the EPA and the highest value of DHA (11.90%) was obtained in the fresh samples. Differences in the values of EPA were not significantly associated (P>0.05) with treatments in contrast to DHA that had significantly decreased values (P<0.05) accounted for by both treatments. In *Penaeus van*namei, eicosapentaenoic acid increased levels (4.22-4.86 %) observed were little compared to reduced values recorded for DHA (3.07-2.60 %) as radiation doses increases in the work of Abreu et al. [2010]. Therefore, heat treatments when applied to shrimp may result in two contrasting scenarios for these important omega acids.

The highest ratio between the omegas of 13.01 was attained in the smoked specimen while the sundried and fresh specimen had 8.16 and 7.76, respectively. The ω -3/ ω -6 in this study were higher to those reported for *Nephrops norvegicus* (4.45), *Palinurus vulgaris* (0.96) and *Penaeus kerathurus* (1.44) [Tsape *et al.*, 2010] which we opined may have generally been influenced by reproductive cycle, geographical location, and salinity. Soltan & Gibson [2008] reported high values of 23.4, 13.6, 8.8 and 10.0 in favour of ω -3 for Australia food namely squid, deep sea cod, deep sea bream and blue grenadier, respectively. Sargent [1997] stated that it is important for human health to increase the consumption of fish or fish products, which are rich in PUFAs of the ω -3 family and poorer in PUFAs of the ω -6 family.

Ultimately, the consumers are concerned about the benefit of dietary food to their health. Using the study of Ulbricht & Southgate [1991] the IA and IT were calculated for the shrimp products as 0.58 to 0.71 and 0.20 to 0.26, respectively. Turan et al. [2011] reported atherogenicity and thrombogenicity index values of 1.34 and 0.31, respectively for fresh Brown shrimp (Cragon cragon). Rosa & Nunes [2004] reported IA and IT values range of 0.24 to 0.32 and 0.18 to 0.21 for red shrimp (Aristeus antennatus), pink shrimp, (Parapenaeus longirostris) and Norway lobster (Nephrops norvegicus) in summer and winter. Arising from this study, eating more of smoked shrimp would make the diet more atherogenic since the order of atherogenicity was smoked > fresh > sundried. Similarly, smoked shrimp was: the most antithrombogenic, followed by fresh and sundried products.

The amino acid composition of the wild black tiger shrimp and specimens of the shrimp subjected to smoking and sun drying is given in Table 3. Essential amino acids, semi essential amino acids and non-essential amino acids were detected in the fresh and preserved specimens. Lysine, glutamate and serine were not significantly different (P>0.05) but values of other amino acids were significantly (P<0.05) affected by the preservation methods adopted in the present study compared to the fresh specimens of the shrimp.

Glutamate (158 mg/g) was the most abundant with the highest value obtained in the sundried products. Similarly, Yanar & Celik [2006] reported glutamic acid to be the most abundant in *Penaeus semisulcatus* (mean=3.18 g/100 g) and *Metapenaeus monoceros* (mean=3.23 g/100 g). In this

TABLE 3. Amino acids composition in raw, smoked and sundried Penaeus monodon.

A	Fresh		Smoked		Sundried	
Amino acids	g/100 g	mg/g protein	g/100 g	mg/g protein	g/100 g	mg/g protein
Glycine	4.34±0.01	66	3.93±0.02	62	3.98±0.00	58
Alanine	3.53 ± 0.01	54	3.71 ± 0.01	58	3.37 ± 0.02	49
Serine	2.77±0.01a	42	2.30 ± 0.03	36	2.69±0.21a	39
Proline	5.17 ± 0.00	79	4.29 ± 0.01	68	4.74 ± 0.00	69
Valine	2.36 ± 0.01	36	2.54 ± 0.00	40	2.75 ± 0.00	40
Threonine	3.48 ± 0.03	53	3.71 ± 0.01	58	3.62 ± 0.01	53
Isoleucine	2.90 ± 0.00	44	2.31 ± 0.01	36	2.24±0.01	33
Leucine	4.50 ± 0.03	68	4.44 ± 0.01	70	5.26 ± 0.02	77
Aspartate	6.71 ± 0.01	102	6.17 ± 0.06	97	6.03 ± 0.02	88
Lysine	$4.03 \pm 0.00^{\circ}$	61	$2.78\pm0.00^{\circ}$	44	$3.63 \pm 0.00^{\circ}$	53
Glutamate	$9.11 \pm 0.00^{\circ}$	138	$9.40\pm0.00^{\circ}$	149	$11.00\pm0.00^{\circ}$	158
Methionine	2.78 ± 0.00	42	1.85 ± 0.01	29	2.16 ± 0.00	32
Phenylalanine	2.54 ± 0.01	39	2.64 ± 0.02	42	3.14 ± 0.01	46
Histidine	1.90 ± 0.00	29	2.37 ± 0.01	37	2.65 ± 0.01	39
Arginine	4.11 ± 0.01	62	3.94 ± 0.01	62	4.86 ± 0.01	71
Tyrosine	2.21 ± 0.00	34	2.88 ± 0.00	45	2.82 ± 0.01	41
Cystine	3.37 ± 0.01	51	4.28 ± 0.02	67	3.68 ± 0.00	54
Total	65.81		63.54	1000	68.62	1000
ΣΕΑΑ	28.6		26.58		30.31	
Σ NEAA	37.21		36.96		38.31	
EAA/ NEAA	0.77		0.72		0.79	

Values are given as means \pm SD from triplicate determinations of three independent experiments. N.B Except otherwise stated means were significantly different (P<0.05) at 0.05 and 0.01 among treatments subjected to ANOVA and LSD.* ANOVA produced no results, no variation amongst the replicate and treatments. Means not significantly different between treatment (P<0.05). Amino Acids Score and Protein Digestibility Corrected-Amino Acid Score for fresh, smoked and sundried *Penaeus monodon*. Reference amino acid pattern of preschool children (2–5 years) FAO/WHO/UNU [1985] and FAO [1991] for histidine. PDCAAS= Protein Digestibility Corrected-Amino Acid Score at 95%.

study glutamate value was increased but not significantly (P>0.05) by both smoking and sun-drying processes. Similar observations were reported for raw, fried, grilled and steamed anchovy (1.325 mg/100 g, 2.418 mg/100 g, 3.379 mg/100 g, 2.120 mg/100 g), small bluefish and medium blue fish [Erkan et al., 2010] while in raw rainbow trout (1901.2-3815.7 mg/100 g) significantly increased (P<0.05) contents of the acid were reported after being subjected to conventional and microwave oven-cooking [Unusan, 2007]. The glutamate levels in fin and shell fishes may be increased when subjected to heat treatments.

The high values of glutamate in dried products accounted for higher flavour and taste and market preference in Nigeria. There are substantial numbers of seasoning with shrimp flavours in the markets. Remarkably, the value of glutamate obtained in this study for the sundried specimen was within the 178±19 mg/g amino acid composition of mixed human milk proteins in FAO/WHO/UNU [1985] indicating the possible usefulness of sundried *P. monodon* as an important in-

gredient in the infant food industry. Preserved shrimp is an important and commonly used ingredient in local weaning food formulation in Nigeria.

The fresh shrimp had the highest value of lysine (4.03 g/100 g) nevertheless, smoked shrimp with the lowest value of 44 mg/g would be sufficient to meet 30 mg/kg per day for an adult consuming 60 g of the shrimp thereby preventing pellagra caused by deficiency in niacin, vitamin B [Özden & Erkan, 2011]. Lysine is very important during fish spoilage, since it can produce biogenic amines by decarboxylation (tyramine, agmatine, and cadaverine, respectively) [Erkan, 2004]. The two methods reduced though not significantly (P>0.05) the contents of lysine nevertheless, this is a positive effect of their abilities to control spoilage in shrimp.

Interestingly, serine values in this study were relatively constant with approximately 40 mg/g. Values in *P. monodon* and *P. vannamei* were also around the 40 mg/g [Sriket *et al.*, 2007] and 41 mg/g in the Chinese mitten crab [Chen *et al.*, 2007]. The value from our study also compared favour-

TABLE 4. Amino Acids Score and Protein Digestibility	

	Reference	Content in fresh muscle		Content in smoked muscle		Content in sundried muscle				
Amino acids	(mg/g protein)	(mg/g protein)	Score	PDCAAS	(mg/g protein)	Score	PDCAAS	(mg/g protein)	Score	PDCAAS
Valine	35	36	103	1.1	40	114	1.1	40	114	1.1
Threonine	34	53	156	1.5	58	171	1.6	53	156	1.5
Isoleucine	28	44	157	1.5	36	129	1.2	33	118	1.1
Leucine	66	68	104	1.0	70	106	1.0	77	117	1.2
Lysine	58	61	105	1.0	44	76	0.7	53	91	0.9
Methionine + Cystine	25	93	372	3.5	96	384	3.6	86	344	3.4
Phenylalanine + Tyrosine	63	76	121	1.1	87	138	1.3	87	138	1.4
Histidine	19	29	153	1.5	37	195	1.9	39	205	2.1
Total	328	457			468			468		

Values are given as means ± SD from triplicate determinations of three independent experiments. Reference amino acid pattern of preschool children (2–5 years) FAO/WHO/UNU [1985] and FAO [1991] for histidine. PDCAAS= Protein Digestibility Corrected- Amino Acid Score at 95%.

ably with amino acid composition of mixed human milk proteins [FAO/WHO/UNU, 1985]. Fuke [1994] stated that serine contributes to acceptability of prawns and lobsters, and is an important amino acid necessary for fatty acid metabolism and the immune system [Erkan et al., 2010]. Relatively, higher values were obtained with fin fishes and were affected by methods of cooking and marination [Unusan, 2007; Özden, 2005] but not by both processes of sun-drying and smoking as used in the present study. Objective evaluation of discrepancies in our data against those found in literatures was limited in view of absence of comparable study on effects of heat treatments on fin and shell fishes.

Valine and leucine values were significantly lower statistically (P<0.05) in the fresh samples compared to the preserved specimens however the changes were not pronounced. The fresh specimen of *P. monodon* had significantly higher (P<0.05) concentration of isoleucine, aspartate, methionine, glycine and proline compared to the value obtained from the two preservation methods. Although these differences were statistically significant, such changes were very small and lowered values in treatments not associated directly with the two treatments except for methionine and glycine which were significantly reduced (P<0.05) in both processing methods.

We speculated in the first instance that the two heat methods applied which resulted in great reduction of methionine may have resulted from interaction between protein segments resulting from advanced stages of Maillard reaction and hold the views by Kilshaw *et al.* [1982] that this may produce undesirable consequences for nutrition. Secondly we reasoned that since the lowest value (2.78 g/100 g) and great reduction was recorded in the smoke samples, methionine may have being involved in the reaction leading to non-enzymatic browning that occurred as a result of chemical oxidation of phenols [Manzocco *et al.*, 2010] produced in wood smoke. Phenol in smoked products has been receiving considerable attention lately in the food industry.

In other studies [Unusan, 2007; Erkan *et al.*, 2010] methionine levels were increased in the fin fishes subjected to conventional and microwave oven-cooked, frying, grilling and steaming processes (achieved at temperatures of 180-190°C). Autoclaving of powdered infant formula at 105°C after being reconstituted in hot water (80°) produced reduced methionine compared to those prepared by conventional methods [Yeung *et al.*, 2006]. The discrepancies noted with our results on methionine may have been related to the composition of the shrimp and not the temperature.

Glycine values in all forms were higher to the values reported for fresh P. monodon (1182 mg/100 g) and P. vannamei (871 mg/100 g) [Sriket et al., 2007] and were significantly reduced (P<0.05) by the two processing methods used with the greatest decline noted for sun-drying (3.98 g/100 g). Sun--drying was carried out under ambient temperature of 29-31°C in this study and within temperature range (25-30°C) in which sundried fish are susceptible to oxidation during storage and leading to browning in tropical ambient temperatures [Smith & Hole, 1991]. We proposed that since shrimps are known to contain a high level of free amino acids such as glycine, the reduction in sundried form of the shrimp may have been associated with the amino acid involvement in fluorescence and colour production. At 25°C proteins and amino acids interacted with lipid oxidation products to produce browning in the presence of water [Smith & Hole, 1991].

Smoking process resulted in statistically higher values (P<0.05) of alanine, threonine, tyrosine and cysteine compared to both fresh and sundried samples. Only the cystine had well pronounced values that were above the fresh and sundried specimen. The increased availability of these amino acids may be explained by the effects of hot smoking on the interaction within protein segments and hence Maillard reaction. This reaction produced desirable browning colouration, flavour, taste and aroma which were observed in the smoked products over sundried and fresh samples (sen-

sory observations not reported). Smoked product had relatively darker brown colouration, and consistence with a higher level of cysteine was observed. Cysteine is sulphur amino acid and Bastos *et al.* [2012] stated that sulphur-containing Maillard odorants constituted the most powerful aroma compounds and often play, although at trace levels, a dominant role in the flavour of cooked meats.

Arginine and histidine in the muscles of sundried *P. mon*odon were significantly raised (P < 0.05) above values obtained in the fresh and smoked samples. The observed increase we proposed was connected with both arginine and histidine strong affinities for ultraviolet radiation generated in the process of sun drying and consistence with their scavenging attributes for free radicals [Fang et al., 2002]. Based on our study, consumption of sundried shrimp offers dietary advantages for prevention of allergy associated with consumption of seafood products. Sundried shrimps would also find favour in the prevention of many human diseases including cancer, atherosclerosis, stroke, rheumatoid arthritis, neurodegeneration, and diabetes [Fang et al., 2002]. Yankah et al. [1993] found raised histidine level in salted fish when sundried. Histidine is essential for children but its indispensability remains unresolved in healthy adult [FAO/WHO/UNU, 1985].

According to amino acid score (Table 4) none of the referenced amino acid for the fresh was found as limiting in *P. monodon*. This indicated that the proteins from fresh Giant tiger shrimp were well balanced in their essential amino acid composition and therefore it is a high quality protein source. The high qualities of proteins in shrimps and crustaceans generally have been reported [Rosa & Nunes, 2004; Özden & Erkan, 2011]. Similarly, all the referenced amino acids met the 1.0 (Table 4) the highest PDCAAS (Protein Digestibility Corrected Amino Acid Score) value meaning that the fresh muscle of the shrimp protein provides 100% of the reference pattern, which reflects the requirements of a two- to five-year child.

In contrast, lysine was found to be the only limiting factor in the smoked and sundried specimens. In both it was apparent that the heat was responsible for the reduction in the amino acid score for lysine. Cockerell et al. [1972] discussed the Maillard reaction in which the free epsilon amino groups of lysine are particularly susceptible to heat damage, forming addition compounds with non-protein compounds (reducing sugars such as glucose) present in the food stuffs. Based on the PDCAAS values, sundried specimens provides 90% of the lysine as well as other referenced amino acids while consumption of smoked specimen would provide 70% of the required lysine or 40.6 mg/g of the 58 mg/g required. It means that 45 mg/g of adult lysine requirement by adult are met by consuming sundried product but not smoked product. Both sundried and smoked products fell short of the requirement of the two- to five-year old child.

Our result highlighted the usefulness of fresh samples over both sundried and smoked products when considering which form of the shrimp to be added as supplementary/complementary ingredient in weaning food. The usual practice is the use of preserved forms and Ehiri *et al.* [2001] stated that these important ingredients are often added after heat treatment, thus increasing the potential for contamination as

a result of handling and long period of storage. In light of our findings it is not sufficient to give concern to food safety related factors alone which are usually given great accentuated attentions by health personnel, the process through which the ingredients are subjected should be investigated and only the process that assured that important nutritional components are spared should be used.

We indeed showed a significant decrease in methionine and glycine in smoked and sundried products while lysine was limited in the two products and raising concern on their use as a weaning supplement. Fortunately, we hope other ingredients would have compensated for the inadequacies reported. However, more data is required if we are to ensure provision of adequate nutrition to infants using locally available ingredients.

The ratios of essential amino acids (EAA) to nonessential amino acids (NEAA) in black tiger shrimp were close to the average of 0.70 reported by Iwasaki & Harada [1985] but higher ratios were reported in shrimps and lobster [Rosa & Nunes, 2003]. Based on the ratio fresh, smoked and sundried *P. monodon* have adequate nutritional protein.

CONCLUSION

This is the first attempt to provide holistic nutritional evaluation of the three frequently consumed forms of the Giant tiger shrimp against varieties of dietary objectives which they meet. On dry weight bases, protein is the most dominant biochemical constituent of the shrimp and was not affected by processes of smoking and sun-drying whereas lipids, ash, fibre and carbohydrate were impacted by both. Smoked specimen having lowest values of stearic acids may be wholesome in preventing cardiovascular diseases. The MUFAs were higher in the smoked samples. Consumption of the shrimps in the three forms is beneficial to the health of individuals since the $\omega\textsc{-}3$ / $\omega\textsc{-}6$ ratios were high in all.

Smoking increased the concentration of alanine, threonine, tyrosine and cysteine and would perhaps account for sweeter taste of the shrimp over other product forms. Sundried specimens were found to increase the values of histidine and arginine. Isoleucine and methionine were found in the highest concentration in the fresh shrimps and therefore are not affected by smoking or sun drying preservation methods. Lysine values were found to be the lowest in sundried and smoked samples mainly due to the impact of heat.

In general, smoked products offered healthiest advantage with the lowest values of saturated fatty acids, Index of Atherogenicity, Index of Thrombogenicity and the highest ω -3/ ω -6 ratios and bearing in mind goal of reduced coronary heart disease (CHD) in food consumption.

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