Available online at www.sciencedirect.com
SCIENCE DIRECT®
Food Chemistry 97 (2006) 490–497
Food Chemistry
www.elsevier.com/locate/foodchem

Heavy metal contaminants and processing effects on the composition, storage stability and fatty acid profiles of five common commercially available fish species in Oron Local Government, Nigeria

Lucy Eboh [a], Horsfall D. Mepba [b,*], Mayo B. Ekpo [a]

[a] Department of Home Economics, University of Uyo, Uyo, Akwa Ibom State, Nigeria
[b] Department of Food Science and Technology, Rivers State University of Science and Technology, P.M.B. 5080 Port Harcourt, Nigeria

Received 28 February 2005; received in revised form 10 May 2005; accepted 10 May 2005

Abstract

Five commercially available common fish species: catfish (*Chsysichthyes nigrodigitatus*), tilapia (*Oreochromis nilotichus*), ilisha (Ilisha africana), bonga (*Ethmalosa fimbriata*) and mudskipper (*Periophthalmus koelreuteri*) in Oron Local Government Area were evaluated for their content of heavy metals and the effects of salting on nutrient contents, oxidative stability and fatty acid profiles of smoke-dried fish cakes. Concentrations of heavy metals in edible muscle, liver and gill tissues were determined while the oxidative rancidities in unsalted and salted smoke-dried fish cakes, packed in low-density polyethylene (LDPE) bags and stored at 30 ± 1 °C were assessed using peroxide value (POV), thiobarbituric acid (TBA) value, free fatty acid (FFA) contents and sensory evaluation techniques. Generally the analytical data for Cu, Zn and Pb in the muscle, gills and liver of test samples were significantly low. Similarly, insignificant concentrations (<0.001 mg/100 g) of Hg, As, Cr and Cd were obtained in the fish tissues. The protein and lipid contents of the fish cakes ranged from 60.8–63.9% to 7.3–9.1%, respectively. Salting caused minimal reductions in the nutrient contents of the dried fish cakes. The POV, TBA, FFA and taste panel scores were highest during the first week of storage and declined thereafter. Salted smoke-dried samples had higher POV, TBA and FFA values than unsalted samples. Panel preference ratings for flavour/aroma and desirability characteristics of the fish cakes were in the order: *C. nigrodigitatus* > *O. nilotichus* > *E. fimbriata* > *I. africana* > *P. keolreuteri*. Palmitic acid (C16:0) was the predominant saturated fatty acid in the test samples. The *eicosapentaenoic* acid (EPA) contents of unsalted smoke-dried *C. nigrodigitatus* was 4.9%, *Oreochromis niloticus* 6.5%, *Ilisha africana* 2.6%, *E. fimbriata* 5.6% and *P. koelreuteri* 7.64%. The *docosahexaenoic* acid (DHA) contents of salted smoked dried fish were 1.8% (*C. nigrodigitatus*), 4.8% (*O. niloticus*), 9.5% (*I. africana*), 5.5% (*E. fimbriata*) and 12.3% (*P. koelreuteri*).

Keywords: Heavy metals; Composition; Oxidative; Fatty acids

1. Introduction

Marine pollution in the Niger delta region of Nigeria, particularly Oron, has increased due to the indiscriminate discharge of untreated municipal and industrial wastes. Besides, the Niger delta seas serve as a waterway, for transportation, for a vast number of companies and industries sited in the region. Principal among these are the oil prospecting companies with their attendant problems of oil spillages and petroleum hydrocarbons discharged from gas flaring. These precipitate with rain and contaminate the environment and eventually enter the food chain. Heavy metals, such as Cu, Zn, Pb, Hg, As, Cr and Cd, are normal constituents of the marine environment and traces are always found in marine

* Corresponding author.
E-mail address: Mepba12002@yahoo.co.uk (H.D. Mepba).

0308-8146/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.foodchem.2005.05.041

organisms (Johnston, 1976). Thus, people who eat large amounts of fish or shellfish from estuarine or coastal areas that are associated with the chemical industry are at risk of heavy metal poisoning (Mahmood, Naeem, Khan, & Qadri, 1995).

Over 90% of the fish produced in Nigeria comes from the artisanal sector with no access to ice or refrigerated storage. Traditional curing methods, such as sun-drying, salting, and smoking, are used in preserving fish that cannot be sold (Eyabi & Ningo, 1998). Some workers have reported the benefits of salting and smoking of fish (Eyabi & Ningo, 1998; FAO, 1991). In salted-dried and salted-smoked fish, susceptibility to autoxidation is dependent on moisture content, and porosity of packaging materials to oxygen and water vapour (Akande, Knowles, & Taylor, 1991). Besides, the presence of inorganic materials, such as NaCl, has been implicated in accelerating lipid autoxidation (Castell, Maclean, & Moor, 1965). It is well-recognized that oxidation of the lipid fraction of fish muscle tissue is a major cause of deterioration in fatty fish (Hultin, McDonald, & Kelleher, 1982; Nawar et al., 1990; Pryor, Prier, Linghtesey, & Church, 1980; Standsby, 1990). Undesirable changes in colour, flavour and even nutritive value, occur as muscle foods become oxidized (Golkap, Ockerman, Plimpton, & Harper, 1983; Melton, 1983). Decomposition products of lipid hydroperoxides are distributed among the aqueous and vapour phases in accordance with their chemical characteristics. Malonaldelyde (MAL), a water-soluble lipid decomposition product, has been used widely as an indicator of the extent of oxidative deterioration of lipids in muscle foods.

The relative abundance and low-cost of fish, increased awareness, advertising and studies demonstrating the beneficial effects of omega-3 fatty acid in preventing certain diseases, especially cardiovascular disease (Balasubramaniam, Simons, Chang, & Hickie, 1985; Herold & Kinsella, 1986) has increased the consumption of foods rich in these fatty acids. However, not all fish products contain appreciable quantities of $n-3$-fatty acids (Lovell, 1988). Extraction and characterization of fish lipids would provide information on the lipid profile of commercially available fish species.

Studies have demonstrated that diets in which unsaturated fats replace the saturated ones are associated with a low incidence of coronary disease (Fuentes, 1988; Mensink & Katan, 1990). This stems from the fact that polyunsaturated fatty acids of the $n-3$ family, especially eicosapentaenoic acid, influence the production of prothrombotic prostanglandin and thromboxane or are converted into anti-thrombotic prostanglandins (Goodnight, Harris, Connor, & Allingtworth, 1982). Thus, all attempts to reduce the risk of cardiovascular disease emphasize the importance of an increased consumption of fish or fish products, which are rich in polyunsaturated fatty acids of the $n-3$ family and poor in polyunsaturated acids of the $n-6$ family (Blurr, 1989; Sergeant, 1997). The present study evaluates the contents of heavy metals and processing effects on the composition, storage stability and fatty acid profiles of selected important fish species in the Oron Local Government Area of the Niger Delta.

2. Materials and Methods

2.1. Collection of Samples

Five fish species were analysed: catfish (*Chsysichthyes nigrodigitatus*), tilapia (*Oreochromis niloticus*), ilisha (*Ilisha africana*), bonga (*Ethmalosa fimbriata*) and mudskipper (*Periophthalamus koelreuteri*). Twenty to twenty five individuals of each of the species, representing the size range commercially available to customers were collected randomly from local fishermen. Immediately after collection, the different species of fish were separated, washed with distilled water and taken to the laboratory.

2.2. Sample preparation

For heavy metal analyses, each fish specimen was beheaded, eviscerated and filleted, all manually.

Similarly, the liver and gills were severed and separately packed, alongside the muscle which was severed under the dorsal fin. All samples were stored at −20 °C until required.

In a second experiment, the beheaded and eviscerated fish were immediately washed, and divided into two lots with ten samples of each fish species per lot. The first lot was immersed in 40 °C brine solution for 15 min (Eyabi & Ningo, 1998) with slight agitation. After brining, the fish samples were drained for 2–3 min and loaded on a traditional oven and fired by hardwood for 12 h. The second lot was similarly smoke-dried but without brining.

2.3. Chemical analyses

Proximate compositions of salted and unsalted smoked-dried samples were done in triplicate for moisture, protein, lipid, carbohydrate, crude fibre and ash contents, following AOAC (1990) methods. Fifty grammes of each sample were ground in a Kenwood Food processor, Model 917A, England, and sieved to 60 μm size and packed in a low-density polythene bag and sealed. Frozen samples of the liver, gills and muscle, dissected from the dorsal fin, were thawed under running tap water and homogenized in a Moulinex Food processor at high speed. Ten grammes of each hot tissue homogenate (liver, gill and muscle) were weighed into a 150 ml air-tight quick flask with glass stopper. Five (5) ml of conc. HNO_3 and 3 ml of 60% perchloric acid were

added to each sample and digested in a temperature-controlled waterbath at 85 °C. After digestion, the samples were separately filtered using an ashless filter paper and the volumes made up to 100 ml with 0.5% HNO_3, then used for the determination of heavy metals. Heavy metal (Cu, Zn, Hg, As, Cr and Cd) contents of the fish tissues were determined using an atomic absorption spectrophotometer, Unicam Analytical system, Model 919, Cambridge, UK.

2.4. Storage studies

Salted and unsalted smoke-dried fish cakes were divided into two lots of 150 g each and packed in low-density polyethylene bags, and sealed, then stored at ambient temperature (30 + 1 °C) for 12 weeks. Samples were withdrawn initially at 4 week intervals and subsequently at intervals of 2 weeks and evaluated for their oxidative stability. The fish samples were chemically analysed for peroxide value (POV), thiobarbituric acid (TBA) value at 532 nm (Fioriti, Kanuk, & Sims, 1974) as modified by Erdelyl (1983). Free fatty acid contents were determined by a titrimetric method as described by Pearson (1976).

2.5. Fatty acid analysis

Lipid contents of ground smoke-dried salted or unsalted fish samples were extracted by the Soxhlet method using *n*-hexane. Extracted lipid samples were methylated using the modified method of IUPAC (1979) for gas chromatographic analysis. Separations of methylated lipid samples were carried out on a Shimadzu PONA GC chromatograph and a Shimadzu RPR-UI chromatograph processor (Shimadzu Corporation, Kyoto 604, Japan). The operating conditions were as follows:

(a) Column type: capillary column (fused silica gel).
(b) Column temperature. 35 °C/min up to 320 °C.
(c) Injection temperature: 200 °C.
(d) Detector temperature: 250 °C.
(e) Sample size: 2 μl (Shimadzu GC 17 A (PPNA)).
(f) Analysis method: splits injection method.
(g) Split ratio: 1:300.
(h) Carrier gas: helium.
(i) Flow rate: 20 cm^3/min.
(j) Speed: 10 mm/min.
(k) Flame ionization.
(l) Detector (F.ID) H_2 + air.
(m) Initial time 3 min.
(n) Final time 20 min.
(o) Stop time 30 min.

Standard fatty acid methylesters were run under the same conditions and the subsequent retention times used to identify fatty acids in the fish lipid samples.

2.6. Sensory evaluation

Twenty member panels of both students and staff of the Department of Food Science, Unitech, Port Harcourt, who were familiar with sensory attributes of smoke-dried fish, evaluated the stored fish cakes for their taste (flavour/aroma) and desirability characteristics. Fish cakes were evaluated initially after 1 month and, thereafter, at 2 weekly intervals, for their sensory characteristics. Panel lists, rated the samples on a 5-point quality scale with 5 = excellent, 4 = very good 3 = good, 2 = fair, 1 = bad.

2.7. Statistical analyses

A randomized complete block design was used to evaluate the data for proximate composition and sensory properties of stored fish samples, while a strip-plot experimental design (Milliken & Johnson, 1984) involving samples and storage periods was used to evaluate changes in the physicochemical properties of stored samples. Data for all measurements were subjected to analysis of variance, as outlined by Milliken and Johnson (1984). Fisher's least significant difference test (LSD) was used to identify significant differences among treatment means ($P \leqslant 0.05$).

3. Results and discussion

Table 1 shows the mean concentrations of seven heavy metals (Cu, Zn, Pb, Hg, As, Cr and Cd) in the muscle, gills and liver tissues of the five fish species. Relatively low levels of Cu, Zn and Pb were observed in the tissues of tested fish samples while insignificant concentrations (<0.000/mg/100 g) of Hg, As, Cr and Cd were obtained. The mean level of Cu in the five fish species was 0.001/mg/100 g. Copper levels in the gills ranged from 0.001 mg/100 g in mudskipper, ilisha and tilapia to 0.002 mg/100 g in bonga fish and catfish. A mean concentration of 0.002 mg/100 g of lead was obtained in the muscle, gills and liver tissues of catfish and tilapia. The concentration of zinc in the tissues varied from 0.001 to 0.002 mg/100 g.

The analytical data showed that all the investigated heavy metals (Table 1) were present in the samples. However, values obtained in the present study were considerably lower than the mean value of 0.283 mg/100 g of Cu in tilapia and an observed cobalt mean levels of 0.142 and 0.316 mg/100 g for catfish and ilisha, respectively (Mahmood et al., 1995). The concentration of Hg, As, Cr and Cd in the species analysed were lower than those of other metals, with their mean values of 0.001/mg/100 g. Generally, the analytical data for Cu, Zn, Pb, Hg, As, Cr, and Cd in the muscle, gills and liver tissues of catfish, tilapia, ilisha, bonga fish and mudskipper were

Table 1
Mean values for heavy metal concentrations in the muscle, gills and liver of the fish samples (mg/100 g)

Sample	Location	Copper	Zinc	Lead	Mercury	Arsenic	Chromium	Cadmium
Catfish	Muscle	0.001	0.001	0.0002	<0.0001	<.0001	<0.0001	<.0001
	Gills	0.002	0.001	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
	Liver	0.002	0.002	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
Tilapia	Muscle	0.001	0.001	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
	Gills	0.001	0.001	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
	Liver	0.002	0.002	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
Ilisha	Muscle	0.001	0.002	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
	Gills	0.001	0.0001	0.0001	<0.0012	<0.0001	<0.0001	<0.0001
	Liver	0.001	0.001	0.0001	<0.0011	<0.0001	<0.0001	<0.0001
Bonga	Muscle	0.001	0.002	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
	Gills	0.002	0.001	0.0002	<0.0001	<0.0001	<0.0001	<0.0001
	Liver	0.001	0.002	0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Mudskipper	Muscle	0.001	0.001	0.00011	ND	ND	<0.0001	<0.0001
	Gills	0.001	0.002	0.00012	<0.0001	<0.0001	<0.0001	<0.0001
	Liver	0.002	0.001	0.0002	<0.0001	<0.0001	<0.0001	<0.0001

ND, not detected.
All values are means of two replications.

lower than the values obtained from other water systems in the world (Sidwell, 1981). Zinc in the fish tissue had a range of 3.9–91.6 and 20.0–45.0 mg/kg in the muscle and liver, respectively, while copper concentrations ranged from 0.08–4.1 to 1.1–3.9 mg/kg in the muscle and liver, respectively (ICES, 1988). The disparity between the results of the present studies and the ICES could be explained by the highly industralized nature of North Atlantic seas compared with Oron river.

The proximate compositions of salted and unsalted smoke-dried fish cakes are given in Table 2. The protein and lipid contents of the fish cakes ranged from 60.8% to 63.9% and 7.3% to 9.1%, respectively. Both unsalted and salted smoke-dried mudskipper had a significantly ($P \leqslant 0.05$) higher protein content than salted and unsalted smoke-dried bonga fish, ilisha and tilapia. Differences in values obtained for the carbohydrates, crude fibre and ash contents were non-significant ($P \geqslant 0.05$). Differences in the values were, however, significant at $P \leqslant 0.01$. Salting caused minimal reductions in the compositions of dried fish cakes.

At the low levels of application (40° brix), salting did not significantly ($P \leqslant 0.05$) reduce the composition of smoked dried fish cakes. The result of this study is in agreement with the results of Bykov (1974), Egwele, Sorinmade, and Tababi (1986), Eyabi and Ningo (1998) and Seno (1974). Similarly, Akande et al. (1991) observed that the lipid contents of mackerel increased on drying and smoking as a result of dehydration. Differences in values obtained for the moisture and lipid contents of treated samples were non-significant ($P \geqslant 0.05$).

Table 3 shows changes in the physicochemical characteristics of salted and unsalted smoke-dried fish cakes at ambient (30 ± 1 °C) temperature storage. The peroxide value (POV), TBA and FFA content were highest

Table 2
Proximate compositions of salted and unsalted smoke-dried fish cakes

Sample	Moisture (%)	Protein (%)	Lipid (%)	Carbohydrate (%)	Crude fibre (%)	Ash (%)
SUC	11.4[a]	62.5[a]	9.10[a]	2.7[a]	3.50[a]	10.8[a]
SSC	11.1[a]	62.3[a]	9.0[a]	2.8[a]	3.3[a]	11.5[a]
SUT	12.6[a]	61.8[a]	7.8[c]	2.5[a]	3.4[a]	11.9[a]
SST	11.8[a]	61.4[b]	8.2[a]	2.6[a]	3.5[a]	12.5[a]
SUI	11.2[a]	61.4[a]	7.4[a]	3.5[a]	4.3[a]	12.2[a]
SSI	11.5[a]	61.3[a]	7.6[a]	3.4[a]	4.2[a]	12.0[a]
SUB	13.1[a]	60.9[a]	7.6[a]	2.6[a]	3.2[a]	12.6[a]
SSB	13.2[ab]	60.8[a]	7.3[a]	2.5[a]	3.4[a]	12.8[a]
SUM	10.2[a]	63.9[ab]	8.7[a]	3.5[a]	3.4[a]	10.3[a]
SSM	10.4[a]	63.6[ab]	9.0[a]	3.1[a]	3.3[a]	10.6[a]
	LSD = 2.8					

SUC, unsalted smoke-dried catfish, SSC, salted smoke-dried Catfish; SUT, unsalted smoke-dried Tilapia: SST, salted smoke-dried Tilapia; SUI, unsalted smoke-dried Ilisha; SSI, salted smoke-dried Ilisha; SUB, unsalted smoke-dried Bonga fish; SSB, salted smoke-dried Bonga fish; SUM, unsalted smoke-dried Mudskipper, SSM, salted smoke-dried Mudskipper.
[a–c] Means in the same column not followed by the same superscripts are significantly ($P \leqslant 0.05$) different.

Table 3
Changes in the physicochemical characteristics of salted and unsalted smoke-dried fish cakes during storage at ambient temperature (30 ± 1 °C)

Samples	Storage periods (weeks)									
	Salted smoke-dried					Unsalted smoke-dried				
	0	1	4	8	10	0	1	4	8	10
POV (meq 0_2/kg oil)										
Catfish	6.8^{a}	85.4^{h}	70.2^{f}	60.1^{d}	40^{b}	6.4^{a}	83.6^{g}	68.4^{e}	56.0^{c}	38.7^{b}
Tilapia	6.4^{a}	78.4^{g}	64.3^{e}	55.3^{d}	34.8^{b}	6.2^{a}	76.9^{f}	63.1^{e}	46.6^{c}	33.9^{b}
Ilisha	6.6^{a}	82.6^{h}	68.6^{f}	52.4^{d}	36.4^{c}	6.4^{a}	80.4^{g}	66.4^{e}	52.1^{c}	34.2^{b}
Bonga fish	6.0^{a}	71.6^{g}	57.8^{f}	42.5^{e}	25.6^{c}	6.1^{a}	70.2^{g}	56.5^{f}	58.6^{d}	23.1^{b}
Mudskipper	6.8^{a}	83.1^{g}	68.6^{f}	53.0^{e}	30.1^{c}	6.4^{a}	82.0^{g}	6.9^{f}	50.6^{d}	27.8^{b}
	LSD = 1.6									
TBA (mg mal/kg oil)										
Catfish	10.2^{a}	58.6^{i}	38.6^{g}	32.5^{e}	24.7^{c}	9.8^{a}	56.8^{h}	36.2^{f}	30.6^{d}	23.4^{b}
Tilapia	9.6^{a}	56.0^{h}	34.1^{f}	28.8^{e}	22.9^{c}	9.5^{a}	55.4^{h}	35.6^{g}	25.7^{d}	20.6^{b}
Ilisha	9.6^{a}	56.0^{i}	34.8^{g}	27.2^{e}	21.4^{c}	9.4^{a}	54.8^{a}	32.8^{f}	25.6^{d}	20.6^{b}
Bonga fish	9.4^{a}	55.8^{i}	34.0^{g}	26.8^{e}	21.6^{c}	9.2^{a}	53.7^{h}	33.0^{f}	24.8^{d}	19.6^{b}
Mudskipper	9.8^{a}	58.4^{g}	38.7^{f}	32.4^{d}	29.8^{c}	9.6^{a}	45.8^{f}	36.2^{e}	30.6^{c}	24.1^{b}
	LSD = 0.9									
Free fatty acid (oleic and mg/100 g)										
Catfish	5.4^{f}	7.5^{i}	4.2^{e}	3.4^{c}	2.1^{a}	5.6^{g}	6.8^{h}	3.7^{d}	2.7^{b}	2.1^{a}
Tilapia	4.8^{g}	6.9^{j}	3.8^{f}	3.0^{d}	2.0^{b}	5.0^{h}	6.1^{i}	3.2^{e}	2.6^{c}	1.8^{a}
Ilisha	5.2^{f}	7.0^{i}	4.0^{e}	3.1^{c}	2.0^{a}	5.3^{a}	6.2^{h}	3.3^{d}	2.7^{b}	2.0^{a}
Bonga fish	4.6^{f}	6.7^{i}	3.6^{e}	2.8^{d}	1.8^{b}	4.8^{a}	6.0^{h}	2.8^{d}	2.3^{c}	1.5^{a}
Mudskipper	5.2^{g}	7.1^{j}	4.0^{f}	3.1^{d}	2.0^{a}	5.4^{h}	6.3^{i}	3.2^{e}	2.7^{c}	2.1^{b}
	LSD = 0.06									

[a,b,c] Means on the same row not followed by the same superscripts are significantly ($P < 0.005$) different.

during the first week of storage and declined during subsequent storage periods. TBA values followed the POV. Generally, the salted smoke-dried fish cakes had significantly ($P \leqslant 0.05$) higher POV, TBA and FFA levels than the unsalted fish cakes.

Although the peroxide value was significantly low at the start of the storage period (week O), the value rose to 85.4 mg/kg oil by the first week of storage and declined during subsequent storage periods. The TBA value, which measures the malonaldehyde (end-product of lipid oxidation) concentration, followed a similar pattern. The increase in TBA values during the first week of storage appeared to be related to oxygen permeability of the packaging material. Brewer, Ikins, and Harbers (1992) reported similar differences in TBA values. Bhattacharya, Hanna, and Mandigo (1988) reported that for 30% fat ground beef, TBA value increased for 12 weeks then decreased slightly over a 30 week storage period. They reported higher TBA values for beef in polythene than vacuum-packaged pork held for the same time in frozen storage. In this study, TBA values increased after the first week, presumably due to the high degree of unsaturation of fish fat, contact of atmospheric air and the high humidity of the storage environment. This trend may reflect the oxidation of PUFA in the phospholipid fraction, followed by oxidation of the neutral lipid fraction. The fact that TBA values showed an apparent decrease during storage suggests that reaction with other flesh constituents may have occurred. Gardener (1979) reported that the end-products of lipid autoxidation can react with proteins and amino acids. Salt is a pro-oxidant and at the 40° brix level used it is thought that it would accelerate autoxidation of lipid. According to Castell et al. (1965), NaCl influences the rate of autoxidation in salted fish by inducing changes in the fish proteins.

Free fatty acids (FFA) are among the hydrolytic products from fish lipids. Lipid hydrolysis can occur with heating or action of enzymes. The lipases, phospholipase A and phospholipase B, are believed to be important enzymes in fish lipid hydrolysis (Hwang & Regenstein, 1993). Varying levels of free fatty acids and 1,2 diglycerides arose from the oxidation of minced mackerel stored under vacuum at 2–3 °C for 15 days and the lipid hydrolysis may affect fish wholesomeness. In this study, brining was observed to influence autoxidation and fatty acid contents of stored fish cakes. The results of this study support those of Lubis and Buckle (1990).

Table 4 presents the eight major fatty aids, (C16:0, C18:0, C18.1, C18:3, C20:1, C20:5, C22:1 and C22:6) obtained in unsalted and salted smoke-dried fish cakes. Among the saturated fatty acids, palmitic acid was the most prevalent in all species with mean values of 8.5% (catfish), 31.9% (tilapia), 36.2% (ilisha), 37.5% (bonga fish) and 9.94% (mudskipper). These values represent contents of unsalted smoke-dried fish cakes. Salting appeared to have caused a slight increase in the fatty acid

Table 4
Fatty acid composition[a] of smoke-dried and salted-dried fish cakes

Fatty Acids	Unsalted					Smoke-dried salted				
	A	B	C	D	E	A	B	C	D	E
C14:0	9.40^{ab}	0.56^{a}	3.40^{a}	0.30^{a}	4.80^{a}	10.7^{ab}	0.60^{a}	3.60^{a}	0.36^{a}	5.4^{a}
C16:0	–	31.9^{b}	36.2^{b}	37.5^{bc}	9.94^{a}	–	32.4^{b}	37.1^{b}	37.6^{bc}	9.94^{a}
C18:0	2.8^{a}	12.8^{ab}	7.46^{a}	15.4^{b}	4.32^{a}	3.12^{a}	13.5^{ab}	7.80^{a}	16.2^{b}	4.55^{a}
C18:1	9.62^{a}	10.6^{a}	11.9^{a}	16.8^{ab}	16.0^{ab}	9.95^{a}	11.0^{a}	12.4^{a}	17.20^{ab}	16.5^{a}
C18:3	14.9^{a}	–	–	–	13.6^{a}	10.4^{a}	–	–	–	13.7^{a}
C20:1	4.52^{a}	0.1^{a}	0.1^{a}	–	13.3^{b}	17.4^{b}	0.4^{a}	2.2^{a}	–	14.1^{b}
C20:5	4.90^{a}	6.50^{a}	2.6^{a}	5.64^{a}	7.64^{a}	4.94^{a}	5.80^{a}	3.70^{a}	6.80^{a}	7.80
C22:1	30.5^{b}	–	–	–	6.41^{a}	30.9^{b}	–	–	–	7.20
C22:6	1.95^{a}	4.90^{a}	8.72^{ab}	4.86^{a}	11.6^{b}	1.80^{a}	4.80^{a}	9.45^{ab}	5.52^{a}	12.3^{ab}
EPA + DHA	6.85	11.4 LDS = 6.8	11.3	10.5	19.2	6.74	10.6	13.2	12.3	20.1

A, *C. nigrodigitatus*; B, *Oreochromis* spp.; C, *Ilisha africana*; D, *Ethmalosa fimbriata*; E, *P. koelreuteri*; Means within the same row not followed by same superscripts are significantly ($P \leqslant 0.05$) different.

[a] =mq/100 g of total fatty acid.

composition of the cakes although differences in the values obtained in few cases are non-significant ($P \leqslant 0.05$). *O. niloticus*, *I. africana*, and *E. fimbriata* (bonga fish) were deficient in C18: 3 (α-linolenic acid) while *E. fimbriata* had insignificantly low levels of C20:1. All tested fish samples had varying levels of C20:5 and C22:6. Significantly different ($P \leqslant 0.05$) levels of C22:1 were obtained in *C. nigrodigitatus* and *P. koelreuteri*.

Salting appeared to have facilitated the elaboration of fatty acid contents of the fish oils. The lipids of marine fish are characterized by their high proportion of polyunsaturated fatty acids, such as the nutritionally important EPA and DHA, which are highly susceptible to autoxidation because of their high degree of unsaturation (Gunstone & Norris, 1983). The results of this study show that the fish samples contained moderate levels (2.6–7.8 mg/100 g) of EPA and significantly ($P \leqslant 0.05$) high levels of DHA. *C. nigrodigitatus* had a significantly ($P \leqslant 0.05$) high content (30.5%) of C22:1 (Gadoleic acid) but lower levels (1.95%) of EPA. According to Lovell (1988), not all fish products contain appreciable quantities of EPA. Besides, nutrition of the fish plays a significant role in the contents of EPA or DHA (Morris, Haynes, Keeton, & Gatin, 1995). For the salted fish cakes, contents of EPA + DHA were *C. nigrodigitatus* 6.15%, *O. niloticus* 10.4%, *I. africana* 13.2%, *E. fimbriata* 12.3% and *P. Koereuteri* 20.1%. Eicosapentaenoic acid (EPA) was the main polyenoid fatty acid found in the *Curimbata* spp. When the species under analysis was the tilapia, EPA prevailed. According to Jauncey (1982), tilapia is a species that requires fatty acids of the $n-6$ family instead of $n-3$ for its nutrition.

Data in Table 5 show panel mean scores for taste (flavour/aroma) and desirability of stored fish cakes. Panel ratings of the fish cakes varied significantly ($P \leqslant 0.05$) within treatments (unsalted and salted samples) and decreased significantly as storage periods progressed. Panel preference ratings for flavour/aroma and desirability attributes of the fish cakes were in the order: A > B > D − C − E. Unsalted fish cakes were rated significantly higher than the salted samples for the tested attributes. Panel scores of salted samples of E (*P. koelreuteri*) dropped significantly between good and fair ratings by the sixth week of storage. Similarly, panel scores for all samples were within the range of fair and bad by the eighth week of storage.

In general, rancid odour and flavour development increased over time at room temperature storage. Although all samples were packed in low density polyethylene bags, rancidity appeared to be related to oxygen permeability of the packaging materials. Although brining enhanced the flavour and appearance of stored samples it was also important in predisposing samples to rancidity because salt is a pro-oxidant (Castell et al., 1965). The observed reduction in lipid oxidation of smoke dried fish cakes may be explained in terms of oxygen barrier properties of polyethylene package and the antioxidant properties of the smoke. Oxidation was observed to be more pronounced in fish samples with the highest concentration of polyunsaturated fatty acids (PUFA), especially the $n-3$ and $n-6$ fatty acids. Polyunsaturated fatty acids are highly sensitive to oxidation because their high degree of unsaturation can be initiated enzymatically by microsomal enzymes, lipoxygenase and peroxidase (Eun, Hearnsberger, & Kim, 1993). Apart from the fatty acid composition, other endogenous factors, such as pH and water activity (Khayat & Schwall, 1983) influence lipid oxidation in food. However, traditional drying methods, as applied in this study, ensure significant reduction of moisture contents to achieve shelf-stable fish cakes. Oxidations in traditional smoke-dried fish are often associated with contact with air and relative humidities of storage environments (Eyabi & Ningo, 1998). Unsalted and salted smoke-dried fish cakes held at ambient temperature storage remained wholesome for six weeks.

Table 5
Panel mean scores for flavour/aroma and desirability characteristics of unsalted and salted smoke-dried fish cakes during storage at ambient temperature

Storage period (weeks)	Samples	Flavour/aroma		Desirability	
		Unsalted	Salted	Unsalted	Salted
1	A	4.5^{r}	4.3^{q}	4.4^{r}	4.3^{p}
	B	4.3^{q}	4.1^{p}	4.2^{q}	4.1^{o}
	C	4.1^{o}	4.0^{o}	4.0^{o}	4.0^{n}
	D	4.2^{p}	4.1^{p}	4.1^{p}	4.1^{o}
	E	3.9^{m}	3.6^{m}	3.9^{n}	3.8^{m}
4	A	4.0^{n}	3.9^{n}	4.0^{o}	3.8^{m}
	B	3.8^{m}	3.5^{i}	3.8^{m}	3.6^{l}
	C	3.6^{k}	3.4^{k}	3.4^{l}	3.0^{j}
	D	3.7^{j}	3.5^{i}	3.6^{k}	3.3^{k}
	E	3.4^{j}	3.2^{j}	3.0^{l}	2.8^{i}
6	A	3.4^{j}	3.2^{i}	3.3^{j}	3.0^{j}
	B	3.2^{i}	2.8^{i}	3.0^{i}	2.7^{h}
	C	3.0^{g}	2.5^{g}	2.8^{g}	2.4^{f}
	D	3.1^{h}	2.7^{h}	2.9^{h}	2.6^{g}
	E	2.7^{f}	2.3^{f}	2.6^{f}	2.3^{e}
8	A	2.1^{e}	1.7^{e}	1.9^{e}	1.6^{d}
	B	1.9^{d}	1.6^{d}	1.8^{d}	1.4^{c}
	C	1.6^{b}	1.3^{b}	1.3^{b}	1.3^{b}
	D	1.7^{c}	1.5^{d}	1.3^{b}	1.4^{c}
	E	1.4^{a}	1.2^{a}	1.3^{a}	1.2^{a}
	LSD = 0.1				

A, *C. nigrodigitatus*; B, *Oreochromis* spp.; C, *Ilisha africana*; D, *Ethmalosa fimbriata*; E, *P. koalreuteri*.
[a] Means in the same row not followed by the same superscripts are significantly different ($P \leqslant 0.05$).

4. Conclusion

Generally, the analytical data for the contents of copper, zinc, lead, mercury, arsenic, chromium and calcium in the muscle, gills and liver tissues of the samples were lower than values obtained from fish samples from other water systems of the world (Sidwell, 1981). Salting did not significantly ($P \leqslant 0.05$) reduce the nutrient contents of the smoke-dried fish samples. The POV, TBA and FFA values rose during the first week and declined thereafter. The fish samples analysed had moderate levels (2.6–7.8 mg/100 g) of EPA and significantly ($P \leqslant 0.05$) high levels of DHA (1.8–12.3 mg/100 g).

Acknowledgements

The authors are grateful to the Nigerian National Petroleum Company (NNPC) for their assistance with the Shimadzu PONA GC.

References

Akande, G. R., Knowles, M. J., & Taylor, K. D. A. (1991). Rancidity and changes in fatty acid composition of salted smoked mackerel cakes. *Tropical Science, 31*, 55–63.

AOAC. (1990). *Official methods of analysis* (15th ed.). Washington, DC: Association of Official Analytical Chemists.

Balasubramaniam, S., Simons, L. A., Chang, S., & Hickie, J. B. (1985). Reduction in plasma cholesterol and increase in biliary cholesterol by a diet rich in $n-3$ fatty acids in the rat. *Journal of Lipid Research, 26*, 684–689.

Bhattacharya, M., Hanna, M. A., & Mandigo, R. W. (1988). Lipid oxidation in ground beef patties as affected by time-temperature and product packaging parameters. *Journal of Food Science, 53*, 174.

Blurr, M. L. (1989). Fish and cardiovascular system. *Progress in Food and Nutrition Science, 13*, 291–316.

Brewer, M. S., Ikins, W. G., & Harbers, C. A. Z. (1992). TBA values, sensory characteristics and volatiles in ground pork during long-term frozen storage: effects of packaging. *Journal of Food Science, 57*(3), 558–563.

Bykov, V. P. (1974). Opportunities for upgrading fish with lower market value. In R. Kreuzer (Ed.), *Fishery products*. 23 Rosemount Ave, Surrey, England: Fishing of News (Books) Ltd.

Castell, C. H., Maclean, J., & Moor, B. (1965). Rancidity in lean fish muscle, IV. Effects of sodium chloride and other salts. *Journal of the Fisheries Research Board of Canada, 32*, 929–944.

Egwele, A. R., Sorinmade, S. O., & Tababi, S. O. (1986). Nutritional evaluation of traditionally smoked bonga. (*Ethmalosa dorsalis*) and Sawa (*Sardinella durita*) obtained from different markets in Lagos, Nigeria. FAO Fisheries Reort No. 229, pp. 156–160.

Erdelyl, A. (1983). Autoxidation of fatty acids produced from natural fats. In: *Fat Science*. Proceedings of 17th ISF Congress, Budapest.

Eun, J., Hearnsberger, J. O., & Kim, J. M. (1993). Antioxidants, activators and inhibitors affect the enzymic lipid peroxidation system of catfish muscle microsomes. *Journal of Food Science, 58*(1), 71–74.

Eyabi, E. G. D., & Ningo, G. (1998). Effects of brine levels and types of packaging on the shelf live of traditionally smoked sardine (*Sardinella maderensis*). *Nigerian Food Journal, 15*, 46–51.

FAO. (1991). Food and Agriculture Organization. Studies on traditional and improved method of smoking fish. FAO Experts Panel. Consultants on fish technology in Africa. Rome, Italy: FAO.

Fioriti, B. A., Kanuk, M. J., & Sims, K. J. (1974). Chemical and organoleptic properties of oxidized fats. *Journal of the American Oil Chemists Society, 51*, 219.

Fuentes, J. A. G. (1988). Que alimentos convem ao coracao? Hig Aliment *12*(53), 7–11.

Gardener, H. N. (1979). Lipid hydroperoxide reactivity with proteins and amino acids. A review. *Journal of Agricultural and Food Chemistry, 27*, 220.

Golkap, H. Y., Ockerman, H. W., Plimpton, R. F., & Harper, W. J. (1983). Fatty acids of neutral phospholipids: rancidity scores and TBA values as influenced by packaging and storage. *Journal of Food Science, 48*, 829.

Goodnight, S. J., Jr., Harris, W. S., Connor, W. E., & Allingtworth, R. D. (1982). Polyunsaturated fatty acids, hyperlipidemia and thrombosis. *Artherioschlerosis, 2*, 87–113.

Gunstone, F. D., & Norris, F. P. (1983). *Lipids in foods*. New York: Pergamon Press.

Herold, P. M., & Kinsella, J. E. (1986). Fish oil consumption and decreased risk of cardiovascular disease: a comparison of findings from animal and human feeding trails. *American Journal of Clinical Nutrition, 43*, 566–598.

Hultin, H. O., McDonald, R. E., & Kelleher, S. D. (1982). Lipid oxidation in fish muscle microsomes. In R. Marting, G. Flick, Ce Hebard, & D. Ward (Eds.), *Chemistry and biochemistry of marine products*. Westport, C.T.: AVI Publishing Co. Inc.

Hwang, K. T., & Regenstein, J. M. (1993). Characteristics of mackerel mince lipid hydrolysis. *Journal of Food Science, 58*(1), 79–83.

ICES. (1988). International Council for Exploration of the Sea. Baseline study of contaminant in fish and shell fish. Cooperative Research Report, p. 366, Copenhagen: ICES.

IUPAC. (1979). International Union of Pure and Applied Chemists. *Standard methods for the analysis of oils, fats and derivatives* (6th ed.). pp. 96–102.

Jauncey, K. (1982). The effects of varying dietary protein utilization and body composition of juvenile tilapias (*Sarotheredon inosambica*). *Aquaculture, 27*, 43–51.

Johnston, R. (1976). *Marine pollution*. London: Academic Press, p. 705.

Khayat, A., & Schwall, D. (1983). Lipid oxidation in seafood. *Food Technology, 7*, 30.

Lovell, R. T. (1988). Increasing omega-3 fatty acids in farmed catfish. *Aquaculture, 141*(15), 54–55.

Lubis, Z., & Buckle, K. A. (1990). Rancidity and lipid oxidation of dried-salted sardines. *International Journal of Food Science and Technology, 25*, 295–303.

Mahmood, S. N., Naeem, S., Khan, F. A., & Qadri, R. B. (1995). Heavy metals in 15 species of Pakistani commercial fish. *Tropical Science, 35*(4), 389–394.

Melton, S. L. (1983). Methodology for following lipid oxidation in muscle foods. *Food Technology, 7*, 105.

Mensink, R. P., & Katan, M. B. (1990). Effect of dietary fatty acids on serum lipids and liporotein. A meta-analysis of 27 trials. *Arteriosclerosis and Thrombosis, 12*, 911–912.

Morris, C. A., Haynes, K. C., Keeton, J. T., & Gatin, D. M. (1995). Fish oil dietary effects on fatty acid composition and flavour of channel catfish. *Journal of Food Science, 60*(6), 1225–1227.

Milliken, G. A., & Johnson, D. E. (1984). *Analysis of messy data. Designed Experiments* (Vol. 1). Belmont, CA: Lifetime Learning Publications.

Nawar, W., Hultin, H., Li, Y., Xing, Y., Kelleher, s., & Wilhelm, C. (1990). Lipid oxidation in seafoods under conventional conditions. *Food Reviews International, 6*, 647.

Pearson, D. (1976). *The chemical analysis of foods* (seventh ed.). London: Churchill Livingstone.

Pryor, W. A., Prier, D. G., Linghtesey, J. W., & Church, D. F. (1980). Initiation of the autoxidation of polyunsaturated fatty acids (PUFA) by ozone and nitrogen dioxide. In M. Simic & M. Karel (Eds.), *Autoxidation in food and biological systems*. New York: Pil. Plenum Press.

Seno, Y. (1974). Processing and utilization. In R. Kreuzer (Ed.), *Fishery products*. 23 Rosemount Avenue, Surrey, England: Fishing News (Books) Ltd.

Sergeant, J. R. (1997). Fish oils and human diet. *British nutrition, 78*(Suppl. 1), 55–513.

Sidwell, V. D. (1981). *Chemical and nutritional composition of finfish, whale, crustaceans, mollusks and their products*. Washington, DC: NOAA Technical memorandum, NME/SEC-11.

Standsby, M. E. (1990). Deterioration. In M. E. Standsby (Ed.), *Fish oils in nutrition* (pp. 120). New York: Van Nostrand Reinhold.