also observed degradation of fenvalerate by both oxidation and hydrolysis. However, other details were not available.

Metabolism of fenvalerate in rats (Ohkawa et al., 1979) and mice and rats (Kaneko et al., 1981) predominantly followed the oxidation at the 4′-position of the alcohol moiety. Hydrolysis of ester linkage and oxidation at the 2′-position of the alcohol were also recognized as metabolic pathways.

In all these studies, oxidation was identified as the major route of degradation. However, in the present studies the only identifiable route was the hydrolysis of the ester bond to produce II and III. Compound III underwent fast elimination of HCN to produce IV, which was easily oxidized by air or enzymatically by oxidase to yield V. Metabolite VI was probably formed by the enzymatic oxidation of V.

The metabolism studies of fenvalerate with laying hens have been extended to include feeding the compound at levels of 50 and 100 ppm for 4 days. Preliminary data indicate that fenvalerate was efficiently metabolized, and the major metabolic route was the hydrolysis of the ester (Akhtar and Foster, 1982).

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Registry No. I, 51630-58-1; [*carbonyl*-^{14}C]I, 78387-52-7; [*phenoxy*-U-^{14}C]I, 86045-64-9; II, 2012-74-0; III, 39515-47-4; [*phenoxy*-U-^{14}C]III, 86045-63-8; IV, 39515-51-0; V, 3739-38-6; VI, 35065-12-4; VII, 67882-25-1; 4-chlorobenzyl chloride, 104-83-6; potassium cyanide-^{14}*C*, 5373-08-0; (4-chlorophenyl)acetonitrile-*1*-^{14}*C*, 78387-50-5; 2-chloropropane, 75-29-6; 2-(4-chlorophenyl)-3-methylbutyronitrile-*1*-^{14}*C*, 86045-60-5; 2-(4-chlorophenyl)-3-methylbutyric-*1*-^{14}*C* acid, 86045-61-6; 2-(4-chlorophenyl)-3-methylbutyric-*1*-^{14}*C* acid chloride, 86045-62-7; 2-(4-chlorophenyl)-3-methylbutyric acid chloride, 51631-50-6; [*phenoxy*-U-^{14}C]phenol, 73607-76-8; 3-bromobenzaldehyde, 3132-99-8; HCN, 74-90-8.

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Polynuclear Aromatic Hydrocarbons in Some Nigerian Preserved Freshwater Fish Species

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Major polynuclear aromatic hydrocarbon (PNAH) contents of traditionally preserved Nigerian freshwater fish species, *Clarias lazera*, *Sarotherodon niloticus*, *Sarotherodon galileus*, *Tilapia zilli*, and *Hemichromis fasciatus*, were determined. This composition was compared to the PNAH content of oven-dried (OD) and Ife solar (a University of Ife built and designed box-type solar dryer) dried (ISD) fish species. The result showed that ease of drying was dependent on the initial oil content of fish ($r = 0.98$), which was also species dependent. Traditionally smoked (TS) product always had a significantly higher PNAH content ($P < 0.01$) while OD products always had significantly lower values. Traditionally solar dried (TD) and ISD products had values greater than OD but lower than TS. The carcinogenic and mutagenic hydrocarbon concentrations in the smoked products were always 2–10 times higher than products from each other preservation method tested.

Traditional methods of fish preservation are widely used in Nigeria today, since the purchase and maintenance of freezing and/or chilling equipment are beyond the means of most fishermen. The fishes are preserved by two methods, smoking and solar drying. The traditional smoking method is widely used throughout most regions and involves exposing the fish directly to burning wood, which leaves heavy smoke deposits on the resulting product. The method as traditionally practiced in some states of northern Nigeria simply exposes the fish to open sunlight where it may be infested by insects or wind-borne sand. While the fisherman preserves his catch for economic reasons, the Nigerian consumer purchases this fish for its organoleptic qualities of odor, flavor, and appearance. Thus, smoked or solar-dried fish in modern Nigeria

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Table I. Moisture and Oil Content of Traditionally Smoked, Traditionally Solar Dried, Oven-Dried, and IFE Solar Dried Freshwater Fish Species[a]

treatment	fish species				
	African mudfish (*C. lazera*)	Tilapia sp. (*S. niloticus*)	Tilapia sp. (*S. galilaeus*)	Tilapia sp. (*T. zilli*)	*H. fasciatus*
traditionally smoked					
moisture content, %	59.47 (±9.12)	46.24 (±6.40)	51.72 (±6.30)	48.31 (±2.49)	33.41 (±1.55)
oil content, % dry wt	16.50 (±0.76)	10.78 (±0.21)	10.03 (±0.03)	9.96 (±1.10)	3.46 (±0.37)
traditionally solar dried					
moisture content, %	54.78 (±9.91)	44.21 (±5.50)	45.21 (±5.21)	45.68 (±5.62)	30.01 (±6.41)
oil content, % dry wt	16.50 (±0.76)	10.78 (±0.21)	10.03 (±0.03)	9.96 (±1.10)	3.46 (±0.37)
over-dried					
moisture content, %	12.04 (±1.26)	11.11 (±1.99)	10.26 (±1.20)	10.87 (±2.90)	4.48 (±0.56)
oil content, % dry wt	16.50 (±0.76)	10.78 (±0.21)	10.03 (±0.01)	9.96 (±1.10)	3.46 (±0.37)
IFE solar dried					
moisture content, %	12.01 (±2.25)	10.84 (±3.20)	7.25 (±2.10)	11.63 (±2.90)	4.40 (±1.20)
oil content, % dry wt	16.50 (±0.76)	10.78 (±0.21)	10.03 (±0.03)	9.96 (±1.10)	3.46 (±0.37)

[a] Values are means of 50 determinations. Values in parentheses are standard deviations of means.

Table II. Naphthalene Content of Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and Ife Solar Dried (ISD) Freshwater Fish Species[a]

fish species	treatment	naphthalenes, ng/g of fish dry wt				
		naphthalene	2-methyl-naphthalene	1-methyl-naphthalene	C2 isomer of naphthalene	C4 isomer of naphthalene
African mudfish (*C. lazera*)	TS	1.75 (±7.6)	18.01 (±2.1)	19.52 (±2.8)	105.66 (±10.6)	42.63 (±8.3)
	TD	4.40 (±2.6)	23.62 (±2.3)	25.31 (±2.4)	84.25 (±28.4)	43.64 (±3.0)
	OD	4.30 (±2.7)	14.22 (±1.5)	16.22 (±1.6)	47.05 (±23.7)	15.18 (±3.1)
	ISD	7.06 (±4.4)	38.90 (±5.3)	37.45 (±8.4)	161.73 (±42.0)	60.07 (±8.7)
Tilapia sp. (*S. niloticus*)	TS	3.52 (±1.8)	19.96 (±1.6)	25.92 (±1.3)	83.60 (±8.2)	36.89 (±2.7)
	TD	0.96 (±1.0)	2.73 (±0.5)	24.43 (±0.4)	16.64 (±4.1)	18.06 (±8.9)
	OD	1.83 (±0.6)	3.12 (±0.5)	24.26 (±0.5)	14.03 (±4.0)	3.84 (±1.0)
	ISD	0.76 (±0.7)	2.16 (±0.6)	22.92 (±0.3)	26.84 (±8.3)	9.52 (±3.3)
Tilapia sp. (*S. galileus*)	TS	6.30 (±0.2)	24.86 (±3.9)	23.32 (±1.2)	85.16 (±4.4)	74.37 (±5.1)
	TD	7.19 (±0.8)	18.50 (±5.9)	22.16 (±2.1)	98.54 (±19.3)	69.11 (±19.9)
	OD	1.32 (±0.6)	3.84 (±0.5)	24.24 (±1.8)	10.84 (±4.2)	3.88 (±1.6)
	ISD	3.11 (±0.3)	3.41 (±0.1)	20.15 (±1.2)	117.73 (±26.9)	3.64 (±4.8)
Tilapia sp. (*T. zilli*)	TS	4.35 (±1.4)	17.23 (±1.5)	20.66 (±0.6)	88.35 (±4.1)	46.93 (±0.3)
	TD	7.38 (±3.6)	16.23 (±4.2)	22.82 (±0.4)	48.43 (±2.1)	30.23 (±5.6)
	OD	4.42 (±3.3)	14.94 (±2.7)	21.33 (±0.7)	48.43 (±2.1)	4.13 (±1.2)
	ISD	4.16 (±2.6)	3.16 (±2.1)	21.96 (±0.2)	87.30 (±15.2)	8.54 (±2.0)
H. fasciatus	TS	7.88 (±0.7)	18.19 (±5.4)	29.20 (±0.4)	122.91 (±12.6)q	61.41 (±6.7
	TD	7.22 (±0.8)	23.94 (±6.7)	2.76 (±0.3)	82.34 (±18.7)	20.14 (±4.1)
	OD	0.19 (±0.8)	2.33 (±2.1)	3.02 (±0.2)	41.26 (±6.1)	20.94 (±4.6)
	ISD	1.71 (±0.7)	6.42 (±4.8)	3.66 (±0.9)	98.42 (±29.3)	20.98 (±3.5)

[a] Values are means of four determinations. Values in parentheses are standard deviations of means.

Table III. Fluorene Content of Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and Ife Solar Dried (ISD) Freshwater Fish Species[a]

fish species	treatment	fluorenes, ng/g of fish dry wt			
		fluorene	methylfluorene	1,2-benzofluorene	2,3-benzofluorene
African mudfish (*C. lazera*)	TS	15.02 (±3.2)	22.07 (±5.3)	12.47 (±0.8)	6.81 (±1.3)
	TD	2.48 (±1.9)	2.71 (±0.3)	1.26 (±0.4)	1.40 (±0.5)
	OD	3.43 (±1.8)	2.23 (±0.8)	0.72 (±0.4)	0.04 (±0)
	ISD	10.39 (±5.3)	masked	2.16 (±0.2)	0.86 (±0.2)
Tilapia sp. (*S. niloticus*)	TS	15.68 (±0.8)	13.16 (±5.4)	45.16 (±2.1)	20.52 (±0.2)
	TD	1.33 (±0.1)	1.12 (±0.3)	1.40 (±0.6)	0.04 (±0.1)
	OD	2.22 (±0.2)	2.21 (±0.6)	1.26 (±0.7)	0.13 (±0.1)
	ISD	4.16 (±0.2)	4.12 (±1.8)	5.40 (±2.1)	1.88 (±0.6)
Tilapia sp. (*S. galileus*)	TS	9.04 (±1.5)	13.76 (±2.1)	43.50 (±6.2)	24.26 (±1.4)
	TD	1.48 (±1.4)	1.05 (±0.1)	1.35 (±0.5)	0.35 (±0.4)
	OD	2.16 (±1.5)	1.28 (±0.5)	1.40 (±0.2)	0.40 (±0.2)
	ISD	2.59 (±0.6)	1.53 (±0.2)	1.01 (±0.2)	1.54 (±0.2)
Tilapia sp. (*T. zilli*)	TS	13.33 (±1.9)	12.01 (±3.01)	48.93 (±0.8)	16.44 (±1.5)
	TD	2.29 (±1.8)	2.94 (±0.1)	1.33 (±0.1)	1.08 (±0.3)
	OD	3.51 (±3.3)	4.13 (±2.4)	1.70 (±0.4)	0.92 (±0.4)
	ISD	4.43 (±3.8)	4.55 (±2.2)	3.13 (±0.3)	0.60 (±0.6)
H. fasciatus	TS	17.22 (±2.0)	21.75 (±7.0)	56.08 (±3.3)	10.16 (±0.9)
	TD	4.10 (±0.1)	4.24 (±0.1)	2.31 (±0.2)	1.25 (±0.1)
	OD	3.96 (±0.3)	4.21 (±0.3)	1.26 (±0.5)	0.44 (±0.61)
	ISD	3.82 (±0.3)	4.73 (±0.7)	1.82 (±0.3)	0.79 (±0.7)

[a] Values are means of four determinations. Values in parentheses are standard deviations of means.

has become a delicacy and is a valued component of the menu.

Consumption of fish preserved by these methods is high in Nigeria [3 kg/capita in 1980 (FOS, 1980)], yet little is known of contaminants introduced during processing (smoke deposits in smoked fish products and environmental deposits during solar drying). Information is sparce on the level and composition of major polynuclear aromatic hydrocarbons (PNAH) in Nigerian freshwater fishes and the effect of traditional preservation methods on the same.

Since several PNAH's have been implicated as carcinogens or mutagens (Lo and Sandi, 1978), an analysis of the levels of these compounds in traditionally preserved fish was undertaken to determine the major PNAH composition of traditionally preserved freshwater species: African mudfish (*Clarias lazera*) and Tilapia species (*Sarotherodon niloticus, Sarotherodon galileus, Tilapia zilli*), which together comprise 40–50% of smoked fish consumed, and Hemichromis *fasciatus* (15–20% of smoked fish consumed). This composition is compared to the PNAH content of oven-dried and Ife solar (a University of Ife built and designed box-type solar dryer) (Salau, 1982) dried fish species.

MATERIALS AND METHODS

Sample Treatment. Fishes used in the traditional preservation portion of this study were caught in the wild in various locations in Nigeria, ungutted, smoked (TS) or solar-dried (TD) on site, and transported to Ife in the preserved form.

Oven-dried (OD) or Ife solar dried (ISD) fishes were collected from fresh waters in Oyo State of Nigeria, transported live to Ife, and dried immediately slaughtered, by using a Fisher drying oven or the Ife solar dryer.

Traditional smoking techniques vary from ethnic group to ethnic group in Nigeria. The most popular method, which is placing fish on wire gauze in a wood-fired kiln made of a steel drum, was used in this study. The temperature of the gauze was between 250 and 300 °C. The smoking time used was 2 h. (an average of time used by local fishermen), and the carcass temperature recorded for the fish at the end of smoking was 110–120 °C. The traditional solar drying time was 4–6 days in the open air as practiced by Nigerian fisherman. This resulted in a carcass temperature during drying of 50–60 °C. Over-dried fish were subjected to 70 °C for 48 h. Fish prepared in the Ife solar dryer were dried for 36 h (6 h/day) at a temperature of 60–90 °C. Fish of each species and treatment group were placed together, ground finely, and stored at −30 °C until used.

The moisture content in duplicate 1-g samples from each treatment group pool was determined according to AOAC

Table IV. Anthracene Content of Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and Ife Solar Dried (ISD) Freshwater Fish Species[a]

fish species	treatment	anthracenes, ng/g of fish dry wt				
		anthracene	methyl-anthracene	C2 isomer of anthracene	benz[a]-anthracene	dibenz-anthracene
African mudfish (*C. lazera*)	TS	15.14 (±1.8)	113.82 (±16.2)	379.32 (±7.2)	8.28 (±1.7)	14.89 (±1.8)
	TD	0.92 (±0.8)	17.36 (±3.7)	105.41 (±63.6)	0.16 (±0.1)	2.97 (±0.3)
	OD	0.40 (±0.3)	15.70 (±4.3)	66.61 (±5.0)	0.28 (±0.2)	1.00 (±0.7)
	ISD	1.62 (±0.7)	49.41 (±7.5)	282.16 (±44.1)	0.43 (±0.2)	14.98 (±6.9)
Tilapia sp. (*S. niloticus*)	TS	24.72 (±3.8)	132.24 (±28.2)	451.36 (±35.3)	50.08 (±2.9)	39.36 (±0.5)
	TD	0.20 (±0.8)	10.14 (±2.1)	475.50 (±9.3)	0.04 (0)	1.09 (±0.6)
	OD	0.20 (±0.7)	11.24 (±4.6)	58.81 (±2.2)	0.92 (±0.4)	0.95 (±0.9)
	ISD	3.72 (±0.3)	48.32 (±11.9)	218.76 (±39.6)	4.40 (±0.4)	2.44 (±0.4)
Tilapia sp. (*S. galileus*)	TS	22.17 (±0.5)	138.51 (±13.9)	449.98 (±31.0)	58.54 (±3.1)	36.19 (±0.2)
	TD	0.38 (±0.8)	120.91 (±80.6)	230.66 (±4.3)	1.52 (±0.1)	1.49 (±0.6)
	OD	0.20 (±0.2)	8.96 (±5.3)	92.64 (±8.0)	1.04 (±0.1)	2.60 (±0.6)
	ISD	0.78 (±0.3)	6.49 (±5.0)	115.11 (±4.2)	0.48 (±0.1)	2.41 (±0.1)
Tilapia sp. (*T. zilli*)	TS	25.15 (±0.2)	129.29 (±6.8)	462.15 (±31.3)	47.42 (±0.7)	37.46 (±1.5)
	TD	0.36 (±0.4)	15.79 (±5.4)	120.12 (±5.7)	0.25 (±0.1)	1.15 (±0.6)
	OD	0.21 (±0.2)	21.05 (±3.6)	128.91 (±8.6)	0.10 (±0.1)	1.78 (±0.2)
	ISD	1.53 (±1.6)	20.12 (±3.3)	123.56 (±8.3)	0.19 (±0.1)	3.18 (±0.8)
H. fasciatus	TS	30.13 (±5.8)	117.32 (±120.5)	563.16 (±43.2)	53.63 (±6.4)	42.16 (±0.9)
	TD	11.22 (±0.3)	31.70 (±7.2)	321.25 (±90.4)	1.14 (±0.3)	2.69 (±0.6)
	OD	0.75 (±0.2)	41.13 (±5.2)	137.86 (±32.8)	1.19 (±0.2)	ND[b]
	ISD	1.40 (±0.7)	47.56 (±5.1)	269.48 (±84.5)	1.32 (±0.2)	0.66 (±0.3)

[a] Values are means of four determinations. Values in parentheses are standard deviations of means. [b] ND = nondetectable.

(1980). Similarly, the oil content in duplicate 5-g samples was determined by the method of Bligh and Dyer (1959).

PNAH Extraction. PNAH extraction and isolation was as described by Mackie et al. (1980). Five grams of treated sample in quadriplicate, was extracted for oil as described by Bligh and Dyer (1959). Oil fraction was concentrated and applied on a silica column. Elution was carried out as follows: The column was washed with 50 mL of *n*-pentane and then eluted with 100 mL of *n*-pentane–benzene (1:1). The eluted fraction was concentrated and applied to a 20 g of Sephadex LH-20 column and eluted with 150 mL of benzene–methanol (1:1). The second 50-mL eluate was collected, concentrated, and applied to the silicic acid column in pentane. The column was washed with 20 mL of *n*-pentane and eluted with 20 mL of *n*-pentane–benzene (1:1). the eluate was dried under nitrogen and kept in acetone for GC–MS analysis. Reagents used were obtained from Sigma and glass redistilled in our laboratory. Recovery efficiencies were estimated on the basis of fully deuterated anthracene (4.82 ng) and pyrene (11.1 ng) spikes included with samples prior to initiation of extraction. Routine recovery efficiency determined in this laboratory was usually greater than 90% for PNAH standards: indeno[1,2,3-*cd*]pyrene, dibenz[*ah*]anthracene, benzo[*a*]pyrene, benzo[*ghi*]perylene, 7,12-dimethylbenz[a]anthracene, benzo[*k*]fluoranthene, 9,10-dimethylanthracene, chrysene plus triphenylene, anthracene-d_{10}, and pyrene-d_{10}). In this experiment recoveries for anthracene-d_{10} and pyrene-d_{10} was 100% and 96%, respectively.

Mass Spectroscopy. The PNAH's were quantitatively analyzed as described by Mackie et al. (1980). GC–MS analysis was carried out by using a VG micromass 16F mass spectrometer equipped with a VG 2250 data system. The mass spectrometer was coupled to a gas chromatograph (Hewlett-Packard 5880). The sample was introduced via the gas chromatograph equipped with a flame ionization detector. A 25 m × 0.2 mm i.d. methyl silicone quartz capillary column coated with SE-54 (programmed from 100 to 260 °C at 3 °C/min) was used in the gas chromatograph. The instrument parameters were as follows: emission current, 200 μA; ionization voltage, 70 eV; injection port temperature, 300 °C; GC–MS interphase temperature was maintained at 250 °C; helium flow, 0.75 mL/min; volume injected, 2 μL in acetone. Identification of PNAH was based mainly on direct comparison of the mass spectrometer response to 37 PNAH standards. Chrysene was measured with triphenylene, since they gave rise to the same parent ion. The *b*, *k*, and *j* isomers of benzofluoranthene were estimated as a group by using benzo[*k*]fluoranthene as the standard. Similarly, dibenzanthracenes and C2 isomers of benzanthracene/

Table V. Pyrene Content of Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and Ife Solar Dried (ISD) Freshwater Fish Species[a]

fish species	treatment	pyrenes, ng/g of fish dry wt					
		pyrene	C1 isomer of pyrene	cyclopenta-pyrene	benzo[e]-pyrene	benzo[a]-pyrene	indeno-pyrene
African mudfish (*C. lazera*)	TS	25.98 (±18.1)	20.64 (±5.6)	0.56 (±0.2)	8.05 (±7.1)	11.12 (±5.9)	6.40 (±1.8)
	TD	4.10 (±7.2)	2.64 (±0.2)	0.08 (±0.1)	5.48 (±3.9)	1.07 (±0.7)	0.21 (±0.2)
	OD	1.47 (±1.6)	1.47 (±0.3)	0.04 (±0.1)	0.32 (±0.8)	0.24 (±0.9)	<0.004
	ISD	4.38 (±5.4)	3.10 (±0.1)	0.20 (±0.8)	12.63 (±8.0)	4.43 (±2.1)	5.92 (±7.3)
Tilapia sp. (*S. niloticus*)	TS	119.36 (±43.7)	57.44 (±2.5)	21.88 (±2.9)	35.72 (±4.2)	45.20 (±13.7)	5.80 (±1.1)
	TD	1.11 (±2.2)	1.56 (±0.5)	0.04 (±0.1)	1.66 (±1.4)	0.48 (±0.2)	3.02 (±1.3)
	OD	1.12 (±2.5)	1.32 (±0.6)	0.10 (±0.1)	3.16 (±1.5)	1.52 (±0.1)	3.10 (±1.7)
	ISD	11.60 (±5.1)	8.36 (±4.7)	1.24 (±0.6)	3.08 (±1.6)	3.04 (±2.4)	2.04 (±1.7)
Tilapia sp. (*S. galileus*)	TS	120.40 (±24.1)	51.29 (±7.6)	21.76 (±1.5)	35.58 (±3.4)	48.19 (±15.1)	5.89 (±1.3)
	TD	3.82 (±0.7)	3.10 (±0.5)	0.65 (±0.7)	5.02 (±1.1)	0.91 (±0.3)	5.35 (±3.1)
	OD	3.04 (±0.2)	3.88 (±0.3)	0.24 (±0.1)	5.48 (±0.6)	1.44 (±0.1)	2.44 (±0.1)
	ISD	3.83 (±0.7)	3.60 (±0.4)	0.66 (±0.2)	3.71 (±0.5)	1.53 (±0.9)	1.00 (±0.2)
Tilapia sp. (*T. zilli*)	TS	119.80 (±10.8)	53.37 (±2.8)	22.24 (±6.9)	32.51 (±4.6)	49.18 (±12.7)	5.35 (±0.6)
	TD	3.40 (±0.7)	3.34 (±0.3)	0.11 (±0.1)	4.72 (±5.5)	1.12 (±0.8)	0.05 (±0.1)
	OD	2.30 (±0.7)	2.12 (±0.7)	0.10 (±0.1)	0.78 (±0.1)	1.41 (±0.8)	2.27 (±0.4)
	ISD	3.71 (±0.4)	2.24 (±0.1)	0.56 (±0.8)	1.52 (±0.8)	1.26 (±0.6)	2.41 (±0.1)
H. fasciatus	TS	132.88 (±61.1)	20.87 (±3.4)	1.35 (±0.3)	45.24 (±11.4)	66.93 (±12.41)	10.12 (±0.3)
	TD	4.33 (±3.8)	1.17 (±0.7)	0.61 (±0.4)	6.52 (±4.1)	1.11 (±0.9)	0.97 (±0.5)
	OD	3.14 (±2.4)	2.01 (±0.5)	0.19 (±0.2)	1.26 (±0.9)	1.07 (±0.4)	ND[b]
	ISD	2.27 (±2.6)	2.02 (±0.7)	0.31 (±0.1)	2.25 (±0.7)	1.08 (±0.9)	0.46 (±0.1)

[a] Values are means of four determinations. Values in parentheses are standard deviations of means. [b] ND = nondetectable.

phenanthrene have also been estimated as a group.

RESULTS

Tables I–VII summarize the results obtained in this study. Table I shows the extent of drying that was usually achieved by traditional smoking (TS), traditional solar drying (TD), oven-drying (OD) and Ife solar drying (ISD). It can be observed in Table I that the extent of drying, when the moisture content is used as an indicator, was significantly greater in OD and ISD than in TS and TD samples ($P < 0.01$). It also appears that the fat content was related to the extent of drying achieved by all the techniques used here ($r = 0.98$).

Tables II–VII show the concentration of the major PNAH in the TS-, TD-, OD-, and ISD-preserved groups. In all, 37 individuals or groups of isomeric PNAH components were assessed. The total PNAH, carcinogenic hydrocarbons (CCH), and mutagenic hydrocarbon (MTH) concentrations in these fishes are presented in Table VIII. In all methods of preservations used, TS products always had a significantly higher PNAH content ($P < 0.01$), while OD always had significantly lower values. TD and ISD products had values greater than OD but lower than TS. The CCH and MTH concentrations in the smoked products were always 2–10 times higher than that of the product from every other preservation method tested ($P < 0.05$).

DISCUSSION

A comparison of results obtained for the fish species used in this study suggests an ease of drying dependence on the oil content of the fish ($r = 0.98$; Table I). The fatty fish *C. lazera*, which had the highest fat content, formed the least dehydrated product, and *H. fasciatus*, which had the lowest fat content, was the most dehydrated of the species studied ($P < 0.01$). This observation may be due to the binding nature of water in the fish muscle. Water in fatty tissue may be more tightly bound and thus more difficult to remove during the drying process.

The PNAH concentration in the fish species studied suggest a reciprocal relationship to the oil content of smoked fish ($r = 0.94$). The oil content followed the order *C. lazera* > *S. niloticus* > *S. galileus* > *T. zilli* > *H. fasciatus* ($P < 0.01$), while the total PNAH, CCH, and MTH content was essentially the reverse, i.e., *C. lazera* < *S. niloticus* < *S. galileus* < *T. zilli* < *H. fasciatus* ($P < 0.01$). This suggests that the greater the oil content in a fish the less susceptible the fish to pyrolitic changes (Masuda and Kuratsune, 1967), which generate polycyclic hydrocarbons during smoking.

The total PNAH, CCH, and MTH concentration in all freshwater fish species considered was also dependent on

Table VI. Phenanthrene and Thiophene Content of Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and Ife Solar Dried (ISD) Freshwater Fish Species[a]

		phenanthrenes, ng/g of fish dry wt			thiophenes, ng/g of fish dry wt		
fish species	treatment	phenanthranes	cyclopentaphenanthrene	benzo[c]phenanthrene	dibenzothiophenes	C1 isomer of dibenzothiophenes	C2 isomer of dibenzothiophenes
African mudfish (*C. lazera*)	TS	115.14 (±3.7)	5.82 (±1.2)	1.55 (±0.1)	3.78 (±0.2)	8.13 (±0.8)	10.36 (±2.6)
	TD	34.10 (±1.3)	1.61 (±0.5)	0.09 (0)	1.82 (±0.4)	3.55 (±0.1)	6.82 (±1.1)
	OD	11.99 (±0.5)	0.44 (±0.2)	<0.004	2.19 (±0.8)	3.63 (±0.1)	4.98 (±0.9)
	ISD	34.82 (±2.5)	1.57 (±0.6)	0.16 (±0.1)	6.04 (±1.1)	12.63 (±2.7)	15.57 (±5.4)
Tilapia sp. (*S. niloticus*)	TS	167.28 (±10.3)	29.44 (±1.6)	9.32 (±1.3)	6.80 (±0.3)	10.08 (±0.9)	12.20 (±0.2)
	TD	10.96 (±0.5)	2.22 (±0.5)	0.01 (0)	1.12 (±0.1)	2.20 (±0.1)	3.68 (±0.2)
	OD	15.63 (±0.2)	0.24 (±0.9)	0.18 (±0.1)	1.26 (±0.2)	2.64 (±0.1)	4.72 (±0.7)
	ISD	32.20 (±0.4)	2.60 (±0.5)	0.92 (±0.1)	5.00 (±1.3)	10.44 (±2.3)	14.36 (±8.6)
Tilapia sp. (*S. galileus*)	TS	189.28 (±2.1)	19.17 (±0.5)	9.11 (±1.0)	7.86 (±0.1)	6.44 (±0.4)	12.23 (±0.1)
	TD	10.51 (±0.5)	1.29 (±0.2)	0.11 (±0.1)	1.99 (±0.8)	3.56 (±0.2)	10.47 (±0.7)
	OD	10.32 (±0.7)	0.24 (±0.7)	0.16 (±0.1)	1.36 (±0.7)	2.80 (±0.2)	7.60 (±0.3)
	ISD	8.56 (±0.5)	0.52 (±0.6)	0.24 (±0.1)	1.13 (±0.1)	2.91 (±0.9)	8.14 (±0.2)
Tilapia sp. (*T. zilli*)	TS	178.87 (±3.4)	23.65 (±1.7)	8.92 (±0.7)	2.80 (±0.6)	8.19 (±0.1)	7.41 (±0.3)
	TD	9.02 (±0.6)	1.81 (±0.8)	0.18 (±0.2)	1.04 (±0.1)	3.40 (±0.4)	7.04 (±0.8)
	OD	11.01 (±0.7)	0.20 (±0.7)	0.42 (±0.1)	1.41 (±0.1)	2.46 (±0.5)	6.14 (±0.8)
	ISD	24.10 (±3.4)	0.89 (±0.7)	0.08 (0)	2.22 (±0.7)	3.65 (±0.7)	10.91 (±0.5)
H. fasciatus	TS	188.19 (±3.3)	7.30 (±2.6)	1.85 (±0.3)	8.97 (±0.2)	8.26 (±0.9)	15.11 (±0.5)
	TD	28.44 (±3.5)	2.30 (±0.3)	1.24 (±0.5)	2.13 (±0.8)	4.27 (±0.3)	5.19 (±0.1)
	OD	20.75 (±0.4)	0.82 (±0.1)	0.19 (±0.1)	3.96 (±0.1)	6.67 (±0.4)	8.62 (±0.3)
	ISD	18.16 (±0.9)	0.08 (±0.1)	0.15 (±0.1)	3.54 (±0.5)	1.15 (±0.7)	13.71 (±0.6)

[a] Values are means of four determinations. Values in parentheses are standard deviations of means.

the method of preservation ($P < 0.01$) for PNAH, $P < 0.05$ for CCH and MTH). Values obtained in the present study are in the range reported by other workers (Lo and Sandi, 1978). The level of PNAH, in general, has been found to be higher in the smoked Nigerian freshwater fish species than in smoked United Kingdom fish (McGill et al., 1981) but similar values to those reported for Japanese fish product (Masuda and Kuratsume, 1971; Masuda et al., 1966).

Preserving fish at a low temperature (70 °C for 48 h in a closed environment (OD) appears to reduce formation of polycyclic hydrocarbons. The drying temperature (50–60 °C) used in TD procedures that was expected to produce lower levels of PNAH produced a significantly higher level than that of OD fish ($P < 0.05$). This could be due to exposure of fish in the open while drying. Contaminants from the environment may have contributed to those elevated levels found (Blumer and Youngblood, 1975). The higher values obtained with ISD fish may be due to higher drying temp. encountered (60–90 ° C) and/or contaminants from the environment as the Ife solar dryer was not sealed from draught. The PNAH concentrations in TS fish that were higher than any other method used could be due to the high temperature (250–300 °C) of smoking, which might generate more pyrolytic products from both wood and fish sources (Masuda and Kuratsune, 1967).

Individual carcinogenic and mutagenic hydrocarbon concentrations were also in close agreement with values reported for U.K. and Japanese fish products (Lo and Sandi, 1978). Although the toxicological implications of these significant concentrations of PNAH are not clear, the levels reported here in the TS fish should be of concern. This is especially true in light of the accumulation of reports that implicate PNAH in a number of carcinomas of the gastrointestinal tract (Lo and Sandi, 1978). Since the TS fish examined in this study are considered lightly smoked, heavily smoked fish may contain even higher concentrations of carcinogenic and mutagenic PNAH. Most traditionally smoked fish in the local market are exposed to smoke for longer periods than used here.

In order to increase the shelf life of smoked fish, fish vendors may resmoke the fish many times until it is sold–increasing the formation of PNAH components (Masuda and Kuratsune, 1967). Therefore, higher levels of these potentially toxic PNAH can be expected in fish sold in local markets than those reported.

An immediate suggestion that arises from this study is that the government of Nigeria should consider the establishment of maximum allowable levels of PNAH in

Table VII. Other Analyzed Polynuclear Aromatic Hydrocarbon Concentrations (ng/g) in Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and IFE Solar Dried (ISD) Freshwater Fish Species[a]

		polynuclear aromatic hydrocarbon, ng/g of fish dry wt										
fish species	treatment	biphenyls	acenaphthylene	benzacenaphthylene	chrysene + triphenylene	C1 isomer of chrysene	C2 isomer of chrysene	fluoranthenes	benzofluoranthenes	perylene	benzoperylene	$C_{18}H_{10}$ (unknown)
African mudfish (*C. lazera*)	TS	23.94 (±4.0)	3.55 (±0.9)	4.42 (±1.6)	14.46 (±5.7)	12.39 (±4.0)	50.28 (±14.44)	34.54 (±5.2)	10.64 (±1.5)	7.33 (±1.2)	7.89 (±1.5)	1.91 (±0.1)
	TD	80.21 (±5.6)	2.41 (±0.1)	0.32 (±0.3)	5.76 (±6.6)	5.81 (±2.5)	30.19 (±5.1)	6.74 (±2.5)	11.48 (±1.3)	0.22 (±0.1)	1.13 (±0.2)	0.41 (±0.4)
	OD	12.71 (±3.7)	0.40 (±0.3)	0.32 (±0.6)	1.71 (±0.4)	3.86 (±2.7)	27.13 (±4.3)	5.26 (±2.2)	0.72 (±0.9)	<0.004	0.40 (±0.4)	0.24 (±0.2)
	ISD	masked	2.24 (±1.7)	ND[b]	7.84 (±2.6)	6.59 (±2.1)	masked	13.92 (±5.9)	18.12 (±5.4)	2.47 (±0.9)	6.12 (±3.1)	0.71 (±0.3)
Tilapia sp. (*S. niloticus*)	TS	25.72 (±3.3)	5.96 (±1.3)	37.56 (±6.1)	54.72 (±4.8)	33.56 (±12.3)	masked	95.04 (±20.5)	10.04 (±1.1)	10.24 (±0.3)	50.08 (±8.7)	7.76 (±6.7)
	TD	7.16 (±3.1)	0.78 (±0.3)	0.41 (±0.8)	1.32 (±0.6)	3.21 (±4.2)	11.60 (±5.7)	6.14 (±3.8)	0.97 (±0.7)	0.01 (±0.2)	1.18 (±0.4)	0.08 (±0.1)
	OD	3.77 (±4.5)	0.26 (±0.6)	0.82 (±0.1)	6.88 (±1.7)	7.91 (±2.8)	15.20 (±4.2)	4.86 (±0.4)	4.12 (±0.3)	0.65 (±0.3)	0.66 (±0.4)	0.64 (±0.9)
	ISD	5.52 (±4.7)	0.44 (±0.2)	2.40 (±1.9)	7.00 (±1.3)	7.12 (±2.3)	24.64 (±4.7)	14.64 (±5.6)	8.80 (±0.5)	0.60 (±0.3)	3.64 (±0.1)	2.68 (±0.6)
Tilapia sp. (*S. galileus*)	TS	46.28 (±6.0)	6.19 (±4.0)	38.47 (±5.4)	56.76 (±4.8)	42.62 (±5.7)	masked	124.35 (±32.2)	9.64 (±0.3)	11.20 (±0.6)	48.21 (±8.2)	6.49 (±8.8)
	TD	43.84 (±5.1)	5.91 (±2.0)	0.01 (±0.3)	4.22 (±0.1)	22.31 (±5.7)	12.25 (±4.6)	7.18 (±1.3)	8.34 (±0.2)	0.04 (±0.01)	1.21 (±0.1)	0.17 (±0.2)
	OD	4.60 (±4.2)	0.24 (±0.8)	0.36 (±0.1)	5.16 (±0.4)	27.81 (±3.3)	19.40 (±4.0)	4.52 (±0.7)	4.72 (±0.2)	0.72 (±0.4)	3.92 (±0.2)	0.08 (±0.1)
	ISD	5.28 (±5.2)	0.41 (±0.5)	0.61 (±0.4)	5.13 (±0.8)	6.01 (±0.4)	15.88 (±4.4)	3.16 (±0.6)	4.41 (±0.9)	0.12 (±0.05)	2.98 (±0.5)	0.04 (0)
Tilapia sp (*T. zilli*)	TS	44.24 (±3.7)	3.91 (±0.4)	33.83 (±6.2)	54.23 (±10.4)	38.83 (±5.4)	141.40 (±156.9)	115.37 (±14.3)	11.20 (±0.9)	8.56 (±0.9)	53.23 (±5.2)	8.91 (±0.6)
	TD	15.47 (±5.5)	3.91 (±0.3)	0.63 (±0.3)	3.82 (±1.2)	3.23 (±6.5)	21.62 (±5.3)	6.34 (±2.1)	4.47 (±0.7)	0.92 (±0.6)	3.24 (±0.5)	0.09 (±0.1)
	OD	4.96 (±3.6)	0.91 (±0.2)	0.41 (±0.4)	2.21 (±0.3)	3.52 (±0.8)	16.12 (±3.8)	5.12 (±0.6)	0.51 (±0.5)	0.23 (±0.1)	1.82 (±0.9)	0.29 (±1.8)
	ISD	3.08 (±4.8)	0.18 (±0.3)	0.56 (±0.7)	4.93 (±1.9)	4.71 (±0.8)	16.05 (±5.1)	6.11 (±0.7)	4.75 (±0.5)	0.51 (±0.1)	1.19 (±0.7)	0.13 (±0.6)
H. fasciatus	TS	42.27 (±5.8)	2.13 (±0.4)	34.43 (±8.8)	44.75 (±5.4)	57.21 (±11.2)	136.56 (±40.7)	140.16 (±6.1)	18.68 (±0.5)	19.21 (±5.1)	82.34 (±4.5)	1.49 (±0.5)
	TD	40.32 (±4.9)	0.91 (±0.2)	5.99 (±3.8)	4.31 (±1.7)	5.13 (±4.9)	33.11 (±5.9)	23.45 (±6.8)	11.26 (±0.4)	1.25 (±1.3)	2.23 (±0.5)	0.63 (±0.1)
	OD	0.38 (±5.1)	<0.004	0.57 (±0.5)	3.08 (±1.1)	3.46 (±0.6)	14.40 (±3.5)	6.04 (±2.4)	3.90 (±0.3)	0.57 (±0.1)	1.13 (±0.1)	0.19 (±0.4)
	ISD	2.45 (±5.3)	<0.004	5.83 (±2.4)	5.59 (±2.0)	4.60 (±0.5)	12.00 (±5.3)	8.08 (±3.3)	4.61 (±0.8)	0.82 (±0.7)	1.28 (±0.6)	0.31 (±0.2)

[a] Values are means of four determinations. Values in parentheses are standard deviations of means. [b] Nondetectable.

Table VIII. Total Polynuclear Aromatic Hydrocarbon (PNAH), Carcinogen, and Mutagen Content of Traditionally Smoked (TS), Traditionally Solar Dried (TD), Oven-Dried (OD), and Ife Solar Dried (ISD) Freshwater Fish Species[a]

fish species	treatment	total PNAH	carcinogen[b]	mutagen[c]
African mudfish	TS	1163.61	204.17	224.63
(*C. lazera*)	TD	522.19	62.58	52.85
	OD	266.90	16.66	21.35
	ISD	826.65	107.76	67.41
Tilapia sp.	TS	1813.37	468.52	556.40
(*S. niloticus*)	TD	614.60	20.73	20.25
	OD	205.78	37.59	31.13
	ISD	527.76	67.24	76.60
Tilapia sp.	TS	1927.37	499.48	619.69
(*S. galileus*)	TD	726.95	38.61	28.54
	OD	245.48	37.84	25.72
	ISD	359.84	30.33	23.47
Tilapia sp.	TS	1995.61	478.01	590.02
(*T. zilli*)	TD	369.32	28.76	24.31
	OD	322.28	22.12	22.36
	ISD	382.16	44.04	41.83
H. fasciatus	TS	2237.50	571.25	656.67
	TD	693.17	59.92	64.00
	OD	340.94	32.95	35.99
	ISD	553.33	36.23	37.90

[a] Values are expressed as ng/g of fish dry wt. [b] Carcinogens include phenanthrene, benz[*a*]anthracene, chrysene plus triphenylene, benzofluoranthenes, benzo[*e*]pyrene, benzo[*a*]pyrene, indenopyrene, benzoperylene, and dibenzanthracene. [c] Mutagens include phenanthrene, anthracene, fluoranthene, pyrene, benza[*a*]anthracene, chrysene plus triphenylene, and benzo[*a*]pyrene (Lo and Sandi, 1978; Poncelet et al., 1978).

smoked fish and encourage the use of oven or solar dryers for preservation of this food. The disadvantage of TD (the cheapest form of preservation) is the heavy sand and disease-carrying insect infestation incurred. The least expensive alternative available is the Ife solar dryer, which provides a hygenic environment and may be constructed with village-level technology at the cost of #120.00 (U.S. $200.00) each. Smoke flavor, free of PNAH, could be introduced to satisfy the consumer organoleptic requirements at relatively low cost.

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Registry No. Naphthalene, 91-20-3; 2-methylnaphthalene, 91-57-6; 1-methylnaphthalene, 90-12-0; fluorene, 86-73-7; methylfluorene, 26914-17-0; 1,2-benzofluorene, 238-84-6; 2,3-benzofluorene, 243-17-4; anthracene, 120-12-7; methylanthracene, 613-12-7; benz[*a*]anthracene, 56-55-3; dibenzanthracene, 414-29-9; pyrene, 129-00-0; cyclopentapyrene, 83381-96-8; benzo[*e*]pyrene, 192-97-2; benzo[*a*]pyrene, 50-32-8; indenopyrene, 72254-06-9; cyclopentaphenanthrene, 80455-52-3; benzo[*a*]phenanthrene, 195-19-7; acenaphthylene, 208-96-8; benzacenaphthylene, 76774-50-0; chrysene, 218-01-9; triphenylene, 217-59-4; perylene, 198-55-0; benzoperylene, 11057-45-7; phenanthrene, 85-01-8; fluoranthene, 206-44-0.

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