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Effect of Sundrying on the Proximate Composition and Lipid Characteristics of Two Freshwater Clupeids

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ABSTRACT

Two freshwater species of clupeids (Pellonula afzeliusi *and* Sierrathrisa leonensis) *found in Kainji Lake, Nigeria, were analyzed to assess their nutritive constituents. The effects of sundrying (the only processing method in the Kainji Lake basin) on the nutrient composition and lipid characteristics of these species were also studied.*

Proximate analysis showed that fresh samples of Sierrathrisa leonensis *and* Pellonula afzeliusi *have crude protein levels of* $14{\cdot}1 \pm 1{\cdot}0\%$ *and* $16{\cdot}0 \pm 1{\cdot}1\%$, *respectively.*

Sundried samples of S. leonensis *contained* $62{\cdot}1 \pm 3{\cdot}2\%$ *protein,* $11{\cdot}0 \pm 1{\cdot}0\%$ *lipid and* $1{\cdot}6 \pm 0{\cdot}2\%$ *ash, while* P. afzeliusi *contained* $57{\cdot}3 \pm 2{\cdot}3\%$ *protein,* $14{\cdot}1 \pm 0{\cdot}9\%$ *lipid and* $2{\cdot}4 \pm 0{\cdot}8\%$ *ash.*

The effect of sundrying was monitored on the extracted lipids of both species. Lipid characteristics, such as iodine value, peroxide value, lipid class composition analysis and fatty acid analysis (by GLC) showed that the lipids underwent lipolysis and autoxidation through sundrying. The analysis calls for a more efficient drying method so that the clupeids could be effectively utilized as sources of protein and good edible fish oil.

INTRODUCTION

Clupeids are the small herrings of the family Clupeidae. They are mostly marine but a few species have colonized the inland waters of the tropical world including major rivers and lakes in Nigeria. According to Reynolds (1969), tropical Africa shelters about 20 species of clupeids but, in Nigeria, only two genera, *Pellonula* and *Sierrathrisa*, are known and have been

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identified in such coastal waters as Benin, Warri and Cross River as well as Lagos and Lekki Lagoons. Reed (1969) identified clupeids in the Niger–Benue river systems and also in Lake Kainji.

According to Otobo & Imevbore (1977), clupeids have a short lifespan but possess a high annual regeneration capacity. In effect, large stocks of unharvestable clupeids are known to abound in the lake and their potential has been estimated at 3000 metric tonnes (Sagua & Otobo, 1976). In the Kainji Lake area, clupeid processing involves simple sundrying and packaging in sacks. Because of their small size and taking advantage of the high ambient temperature, clupeids are sundried within 24–72 h and thereafter packaged in bags and transported to southern markets.

The biochemical characteristics of these clupeids (both fresh and dried) are discussed in this paper. The effects of sundrying on the nutritive characteristics of the lipids, with a view to proposing better processing methods for better utilization of these resources, are also highlighted.

MATERIALS AND METHODS

Collection of clupeids and analytical methods

Clupeids were caught by the research boat of the Kainji Lake Research Institute, New Bussa, Nigeria, by the light attraction method (Otobo, 1974) and using scoopnets to collect them. Catches were separated into the two species, *Pellonula afzeliusi* and *Sierrathrisa leonensis*, using their morphomeric characteristics (Otobo, 1978). The size range for *P. afzeliusi* was 25–55 mm and 22–45 mm for *Sierrathrisa leonensis*.

Fresh samples of each species were kept at $-4°$ to $-5°$C until when they were required for analysis. Whole fish were then homogenized in a Kenwood blender and samples were withdrawn for analysis.

About 2 kg of each species were sundried for 48 h and carefully bagged. These dried samples were also kept at between $-4°$ and —5°C for analysis.

Proximate Analysis

Moisture, ash and nitrogen were determined by the methods of the Association of Official Analytical Chemists (AOAC, 1970). Protein was then calculated by multiplying the nitrogen content by 6·25. Lipid was determined by the chloroform–methanol system of Bligh & Dyer (1959).

Mineral determination (calcium and phosphorus)

Two grams of each sample were oxidized by wet ashing procedure (Perkin-Elmer Inc., 1971) and the calcium determined by atomic absorption

spectrophotometry using a Perkin-Elmer 209 at a wavelength of 423 millimicron. The phosphorus in samples was determined colorimetrically using the phosphovanado molybdate method (AOAC, 1970).

Lipid characteristics

The iodine value, peroxide value and free fatty acids were determined as described by Pearson (1976).

Lipid class analysis
Separation of lipid classes on a single thin-layer plate was carried out by the methods of Freeman & West (1966). The spots on thin-layer plates were scanned in a densitometer and the peaks identified as the various lipid fractions by comparing with those of known standards. Peak area was determined by triangulation.

Fatty acid analysis
Extracted oils of both the fresh and sundried samples of *Pellonula afzeliusi* were methylated (Metcalfe & Schmidt, 1960) for gas chromatographic analysis. The dry heptane solutions of the methyl esters were then injected into a Pye 204 gas chromatograph. Operating conditions were as follows:

Column:	1·5 m × 4 mm glass packed with 25% diethylene glycol succinate (DEGS) on Chromosorb 100/120 mesh
Column temperature:	198°C
Carrier gas:	Nitrogen at 37 ml/min
Detector:	Flame ionization
Detector temperature:	350°C
Attenuation:	10×10^2
Chart speed:	240 s/cm
Solvent:	*n*-heptane (chromatographically pure)

The details of the identification of fatty acids and measurement of peak areas have been described earlier by Balogun & Fetuga (1985).

RESULTS

The proximate composition of the two species of clupeids (both in the fresh and dried forms) is presented in Table 1. The crude protein levels for *Pellonula afzeliusi* and *Sierrathrisa leonensis* are $16{\cdot}0 \pm 1{\cdot}0\%$ and

TABLE 1
Percentage Proximate Composition, Calcium and Phosphorus Content of Fresh and Sundried Clupeids[a]

Species	*Moisture*	*Crude protein*	*Ether extract*	*Total ash*	*Calcium* (%)	*Phosphorus* (%)
Wet						
Pellonula afzeliusi	72·3 ± 3·2	16·0 ± 1·0	3·4 ± 0·2	1·9 ± 0·08	1·7 ± 0·03	0·9 ± 0·05
Sierrathrisa leonensis	73·1 ± 3·4	14·1 ± 1·1	2·1 ± 0·1	1·3 ± 0·04	1·5 ± 0·02	0·9 ± 0·03
Dry samples						
Pellonula afzeliusi	5·5 ± 0·4	57·3 ± 2·3	14·1 ± 0·9	2·4 ± 0·8	3·1 ± 0·04	1·7 ± 0·05
Sierrathrisa leonensis	6·0 ± 0·8	62·1 ± 3·2	11·0 ± 1·0	1·6 ± 0·2	2·6 ± 0·01	1·5 ± 0·03

[a] Average of duplicate determinations.

TABLE 2
Effect of Sundrying on the Lipid Characteristics[a] of *S. leonensis* and *P. afzeliusi*

Species	*Iodine value*	*Free fatty acid (as % of oleic acid)*	*Peroxide value millequiv/kg oil*
Wet samples			
S. leonensis	122 ± 1·0	2·5 ± 0·01	2·0 ± 0·01
P. afzeliusi	126 ± 1·5	2·8 ± 0·01	3·7 ± 0·03
Dry samples			
S. leonensis	80·5 ± 0·9	11·5 ± 0·7	6·4 ± 0·5
P. afzeliusi	91·6 ± 1·1	9·6 ± 0·6	8·9 ± 0·6

[a] Average of duplicate analysis.

14·1 ± 1·1% and 57·3 ± 2·3% and 62·1 ± 3·2% for fresh and dried samples, respectively.

The moisture contents of fresh samples of both species were reduced considerably through sundrying to residual levels of 5·5 ± 0·4% in *P. afzeliusi* and 6·0 ± 0·8% in *S. leonensis*. On the other hand, sundrying elicited significant increases in both the lipid levels and ash levels of both samples with *P. afzeliusi* showing higher levels.

Calcium and phosphorus levels in the dried samples of both species are 2·6 ± 0·01% and 1·5 ± 0·02% for *S. leonensis* and 3·1 ± 0·04% and 1·7 ± 0·05% for *P. afzeliusi*, respectively.

Table 2 presents the effect of sundrying on the lipid characteristics of the clupeids. The iodine value, free fatty acid and peroxide value of wet samples of *S. leonensis* were 122 ± 1·0, 2·5 ± 0·01% and 2·0 millequiv/kg lipid, while those for *P. afzeliusi* were 126 ± 1·5, 2·8 ± 0·01% and 3·7 millequiv/kg lipid, respectively.

The dried samples of both species showed lower iodine values, and higher free fatty acids and peroxide values than the fresh samples.

Effect of sundrying on the lipid class composition is presented in Table 3. In both species, the triglycerides were the lipid class in highest proportion, with levels ranging between 56·5% and 58·9% in the wet samples and 40·5–42·1% in the dried samples. Phospholipids accounted for between 10·5% and 11·8% in the wet, and 7·1% and 8·0% in the sundried, samples. Generally, significantly higher levels of free fatty acids were obtained in the lipids of the sundried samples. Sundrying also produced significant reduction in the triglyceride fraction of both species. However, monoglycerides, which could not be detected in the fresh samples, yielded levels of 5·0% and 6·0% in the dried samples of both species.

The effect of sundrying was evident in the fatty acid composition of the

TABLE 3
Effect of Sundrying on the Lipid Class Composition[a] (%) of *S. leonensis* and *P. afzeliusi*

Lipid class	S. leonensis		P. afzeliusi	
	Wet	*Dry*	*Wet*	*Dry*
Phospholipids	10·5	7·1	11·8	8·0
Monoglycerides	—	6·0	—	5·0
Free fatty acids	3·0	18·1	2·0	14·9
Cholesterol	3·6	3·4	3·1	3·0
Diglycerides	14·8	12·4	16·5	13·2
Triglycerides	56·5	40·5	58·9	42·1
Cholesterol esters	—	—	—	—
Hydrocarbons	—	—	—	—

[a] Average of duplicate determinations.

lipid of *P. afzeliusi* and the results are presented in Table 4. In the wet sample, palmitic acid (16:0) occurred in highest proportion of the saturated acids (34·9%) while oleic acid (18:1) occurred as the most abundant unsaturated fatty acid (29·8%). Of notable importance is the occurrence of polyunsaturated acids such as linolenic acid (18:3), eicosapentanoic acid (20:5) and arachidonic acid (20:4). Trace amounts of docosapentanoic acid (22:5) and

TABLE 4
Effect of Sundrying on the Fatty Acid Composition of the Lipids of *P. afzeliusi*[a]

Fatty acid group	*Composition* (%)	
	Wet	*Dry*
14:0	1·4	4·0
14:1	Trace	0·9
16:0	34·9	36·5
16:1	7·8	9·0
18:0	12·4	13·3
18:1	29·8	33·9
18:2	3·7	1·2
18:3	5·1	0·6
18:4	Trace	—
20:4	0·5	—
20:5	2·3	—
22:1	2·2	2·5
22:5	Trace	—
22:6	Trace	—

[a] Average of triplicate determinations.

docosahexanoic acid (22:6) were also detected. In the sundried sample, palmitic and oleic acids also occurred as the most abundant acids in the lipid but at slightly higher levels than in the fresh sample. Sundrying apparently affected the higher polyunsaturated fatty acids. For example, 20:5, which appeared in trace amounts in the fresh lipids, could not be detected in the lipids of the dried sample.

DISCUSSION

The proximate composition data on the fresh samples of *P. afzeliusi* and *S. leonensis* appear to compare with other freshwater and marine fishes. However, the protein contents of the two species are slightly lower than values reported for *Katsuwonus pelamis* (Balogun & Talabi, 1985) *Trichurus lepturus* (Emokpae, 1980), *Brachydeuterus auritus* (Talabi *et al.*, 1980) and some fresh water species (A. M. Balogun, unpublished). However, the range of lipid content in these two freshwater clupeids classifies them as moderately fatty species in accordance with the classification of Stansby & Oleott (1963). The variability obtained in these two species *vis-à-vis* other species may be related to factors such as size and ecological, physiological and nutritional status of the fish as enumerated by Brown (1957). The clupeids belong to the herring group of fishes and, as such, their moderately fatty nature could enhance their utilization in the canning industry. In this respect, *P. afzeliusi*, because of its bigger size, could be canned in oil, in the same way as the sardine group of fishes is utilized.

Presently, the only form of utilization of the clupeids is in the dried form. They are sundried in the Kainji Lake area and used either as condiments in stew or as whole dried fish in vegetable soup preparations in the Southern States of Nigeria. It is evident, however, that sundrying resulted in a concentration of the nutrients with low residual moisture. This accounted for the high protein contents of the two species. High lipid contents are also encountered in the dried samples of both species. The high protein, coupled with the high lipid content, underlines their potential as high protein–calorie dried fish products. It must, however, be realized that the high lipid content poses a serious threat to storage stability.

When compared with some other dried fish products such as fish meal, the ash levels in the sundried clupeids appeared fairly low and this is an indication that they may not be good sources of the essential minerals. This is evidenced by the relatively low levels of calcium and phosphorus in these samples when compared with values reported for dried fish meal product from Brachy (*Brachydeuterus auritus*) by Talabi *et al.* (1980).

The effect of sundrying on the nature and the characteristics of the lipids

of *P. afzeliusi* and *Sierratherisa leonensis* is evidenced by their iodine values, free fatty acid levels, peroxide values, lipid class changes and fatty acid changes. The lipids of both dried samples showed reduced iodine value, increased levels of free fatty acids (FFA) and peroxide values (PV). Iodine value measures the degree of unsaturation, the free fatty acids (FFA) measure the lipolysis of lipid while the peroxide value (PV) is a measure of the autoxidative processes in a lipid. The fact that substantial reduction occurred in the iodine values and appreciable increases occurred in the FFA and PV of these sundried products, revealed extensive lipolysis by fish muscle lipases and autoxidation of the fish lipids aided by atmospheric oxygen. A lot of minor constituents of the fish may initiate (probably through cation catalysis) lipid autoxidation to yield peroxide radicals, which, in turn, react with the substrate to yield primary hydroperoxides and free radicals. This effect on the lipid is also exemplified by the lipid composition of the sundried products. Although the triglycerides formed the major lipid class, as noted for other species by Hardy & Mackie (1968) and Balogun & Talabi (1984), it should be noted that sundrying caused a substantial reduction in the triglyceride levels in both species. Reduced levels of both triglycerides and phospholipids, with appreciable increase in the levels of the free fatty acids, were also observed. Lipolytic enzymes are known to bind themselves to lipid matrices by means of hydrophobic or electrostatic forces in such a way that their active sites are in close proximity to the lipid ester linkage. Thus, lipolysis of triglycerides and phospholipids is a stepwise process. In the triglyceride, the alpha position is first attacked before the beta position, which is attacked rather more slowly (Constantin *et al.*, 1960). In the phospholipids, the beta-position is first attacked and specific phospholipases (A2-type phospholipase) are necessary for subsequent attack (Desnuelle & Savary, 1963). Such reductions in the triglyceride and phospholipid levels observed with the dried clupeids, and the subsequent increases in the free fatty acid levels, may result from the processes just described. This view is also supported by the work of Watts (1962), Sulzbacher & Gaddis (1968), Bratzler *et al.* (1977) and on the fate of triglycerides and phospholipids in meat and fish flesh.

More evidence on the effect of sundrying, on the lipids of the clupeids, is presented by the GLC analysis of the lipids into their component fatty acids. The fresh lipid of *P. afzeliusi* showed the characteristic fatty acid pattern of fresh water species with high incidence of very highly polyunsaturated fatty acids (20:4–22:6). The importance of these groups of acids in nutrition and health has been extensively discussed (Aaes-Jorgensen, 1961; Ackman, 1974; Holman, 1970). Sundrying in the present instance produced remarkable changes in the fatty acid pattern of the clupeid. Most of the highly unsaturated acids could not be detected. There is, however, a slight

concentration effect for both palmitic and oleic acids. On the other hand, the linoleic and linolenic acid levels were reduced in the dried sample. Fish lipids are highly unsaturated and therefore they are easily predisposed to the type of oxidation processes described above when the lipids are unprotected. In the present circumstances, the disappearance of the 20:4–22:6 group of fatty acids and the reduction in the 18:2 and 18:3 group is due to the autoxidation of very highly reactive ethylenic sites of these acids. Ackman & Eaton (1966), Greene (1969), and Ackman (1974) have all produced evidence to show that autoxidation of highly unsaturated fatty acids is responsible for the development of rancidity and objectionable flavours in fish lipids. When hydroperoxides are produced they may later be further degraded to produce secondary products such as malonaldehyde and other aldehydes and ketones. The so-called rancidity flavour is associated with these secondary products. The accumulation of these secondary products, which were not detected by the present method of analysis, may be partly responsible for the disappearance and reduction of these highly reactive acids.

In conclusion, the compositional data presented in this paper have highlighted the usefulness of the freshwater clupeids as potential industrial biomaterials for canning and as potential sources of high protein–calorie fish food products. However, the numerous problems associated with the sundrying method, already in use in the artisanal sector of the Kainji Lake basin, should be properly investigated with a view to improving the method. Such improvement should take cognisance of the rate of autolysis, lipolysis and autoxidation and possible sand contaminants associated with sun-drying which result in a rancid and poor quality product.

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