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Effect of different cooking methods on the oxidation, proximate and fatty acid composition of silver catfish (*Rhamdia quelen*) fillets

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Abstract

The influence of seven cooking methods (boiling, conventional baking, microwave baking, grilling, deep-frying in soybean oil, canola oil, or partially hydrogenated vegetable oil) on the oxidation, proximate and fatty acid composition of silver catfish (*Rhamdia quelen*) fillets was evaluated. All the treatments reduced moisture and increased the protein content. The free fatty acid content of the fillets was significantly reduced by the different cooking methods, while conjugated diene levels and peroxide values decreased for all fried samples, but remained constant in the samples subjected to the other cooking methods. Boiling and baking increased thiobarbituric acid reactive substances (TBARS), while grilling and frying did not change TBARS. Boiling, baking, and grilling did not affect the silver catfish fillets fatty acid composition. Frying in canola oil increased $n-3/n-6$ ratio, while frying in soybean oil increased the general polyunsaturated fatty acid content, and frying in hydrogenated vegetable oil incorporated trans fatty acids in the fillets.

Keywords: Fish fillets; Boiling; Baking; Frying; Grilling; Lipid oxidation

1. Introduction

The silver catfish (*Rhamdia quelen*) is a freshwater fish, native from Central and South America. It has attracted fish producers and consumers from the south of Brazil, because it has a very good taste, low fat content and is well adapted to fish farming (Luchini & Avendaño, 1985).

Fish has long been recognized as a valuable source of high-quality protein in the human diet. In recent years, fish lipids have also assumed great nutritional significance, because of their high polyunsaturated fatty acid levels (Puwastien et al., 1999). Polyunsaturated fatty acids (PUFA) can reduce blood LDL cholesterol and have antithrombotic, antiinflammatory, antiarrhythmic and vasodilatory properties (Lombardo & Chicco, 2006). Hence, PUFA may help to prevent coronary heart disease, hypertension, type 2 diabetes and insulin resistance.

Studies of nutrients intake from fish, in relation to health, are frequently carried out with data obtained from raw food. However, PUFA content in raw fish tissue may not provide explicit information on the nutritive value of these species after cooking. In Brazil, fish is sometimes eaten raw, but it is usually treated by one of various cooking processes before consumption and these processes can give rise to major changes in composition. The fish species and the cooking method used may be determinant factors for the content of essential fatty acids in the consumed products (Gladyshev, Sushchik, Gubanenko, Demirchieva, & Kalachova, 2006).

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Heating (boiling, grilling, baking, and frying) is applied to food to enhance its flavour and taste, inactivate pathogenic microorganisms and increase shelf life (Bognar, 1998). Some of the major changes that occur during processing and final preparation of heated food are due to oxidation. The PUFA, such as eicosapentaenoic (EPA) and docosahexaenoic (DHA), are considered to be especially susceptible to oxidation during heating and other culinary treatments (Sant'Ana & Mancini-Filho, 2000).

PUFA autooxidation is catalysed by heat, light, trace metals or enzymes and involves free radical generation. Free radicals propagate autooxidation by reacting with oxygen to form hydroperoxides, which breakdown to generate other new free radicals. The hydroperoxides formed can be measured and their concentration used to evaluate the extent of oxidation. Some other measurements can be used to complement the oxidation studies, such as the levels of thiobarbituric acid reactive substances (TBARS), conjugated dienes (CD) and free fatty acids (FFA) (Zuta, Simpson, Zhao, & Leclerc, 2007).

This study was, therefore, conducted to determine the influence of seven cooking methods (boiling, conventional baking, microwave baking, grilling, deep-frying in soybean oil, canola oil, or partially hydrogenated vegetable oil) on the composition (proximate and fatty acid profile) and lipid oxidation of silver catfish (*Rhamdia quelen*) fillets.

2. Materials and methods

2.1. Sample procedures

Samples of silver catfish (*Rhamdia quelen*) were obtained from a local fish farm (Santa Maria, Brazil) during the autumn of 2006. They were eviscerated, washed and immediately transported to the laboratory in ice containing boxes. Fresh fish were washed with tap water several times to remove adhering blood and slime, they were then prepared using common household practices, such as removing head, backbone, skin, tail and fin yielding two fillets (88 ± 17 g each one). The fillets were randomly divided into 24 homogenous portions of ~260 g each, which were assigned to the three repetitions of each one of the seven cooking methods and to the raw group that was used as a reference.

2.2. Cooking methods

Common ways of cooking were used. Boiling was performed at approximately 98 °C (water temperature) for 12 min. The mean core temperature of the silver catfish fillet samples immediately after boiling was 89 ± 9 °C.

To prepare conventionally baked fillets the oven temperature was set at 250 °C for 30 min (pre-heating), then the fillets were baked for 20 min being turned once after 5 min. The mean core temperature immediately after cooking was 77 ± 10 °C.

Microwave-baked fillets were prepared in a domestic microwave-oven (Brastemp – Jet Defrost Crisp) at potency 10, for 2 min. The mean core temperature immediately after cooking was 92 ± 4 °C.

Grilled fillets were prepared in a Black & Decker griller model G48, with the thermostat set at 350 °C. After the set temperature was attained the fillets were grilled for 10 min (5 min on each side). The mean core temperature immediately after grilling was around 76 ± 7 °C.

The fish fillets were deep fried in soybean oil, canola oil, or in partially hydrogenated vegetable oil for 3.5 min. The frying temperature was around 220 °C in the soybean oil and 215 °C in the canola oil and hydrogenated vegetable oil. Mean core temperatures immediately after frying were 91 ± 5 °C, 90 ± 5 °C and 94 ± 3 °C for soybean, canola oil, and hydrogenated vegetable oil, respectively.

Samples of raw or cooked fish fillets were immediately homogenised and used to determine proximate and fatty acid composition as well as the level of free fatty acids, conjugated dienes, peroxide value, and thiobarbituric acid reactive substances (TBARS).

2.3. Analyses

2.3.1. Proximate composition

Proximate composition of cooked and uncooked fish fillets were done in duplicate for moisture, protein, lipid and ash contents. Moisture was determined by the weight loss after 4 h at 60 °C in an assisted air circulation oven, followed by 8 h at 105 °C. The ash content was determined at 550 °C (method 923.03) according to AOAC (1995). The crude protein ($N \times 6.25$) content was determined by the microKjeldahl procedure (method 960.52) of the AOAC (1995). Lipids were extracted from the muscle tissues using the Bligh and Dyer (1959) method and used both for lipid quantification and for determination of the fatty acid profile, peroxide value, conjugated diene and free fatty acid analysis.

2.3.2. Free fatty acids (FFA)

The free fatty acids content was determined, according to Lowry and Tinsley (1976), in the fat extracted by the Bligh-Dyer method (1959). Toluene (2.5 ml) was used as the solvent of choice, 0.5 ml of 5% cupric acetate-pyrydine reagent was added to the tube and shaken for 2 min. The biphasic system was centrifuged for 10 min and the top layer was read at 725 nm. A standard curve, using oleic acid solution, was used to calculate the content of free fatty acid in the fat from the sample.

2.3.3. Conjugated dienes

The conjugated diene value was determined in the fat, extracted by the Bligh-Dyer method (1959), using cyclohexane as the solvent and by recording the optical density (1 cm light path) at 233 nm against a cyclohexane blank (Recknagel & Glende, 1984).

2.3.4. Peroxide value (PV)

The peroxide value was determined in the fat, extracted by the Bligh and Dyer method (1959), using a ferric thiocyanate method according to Chapman and Mackay (1949). No preliminary dilution with a benzene/methanol solution was necessary. A standard curve using ferric iron solution was used to calculate the content of peroxides in the fat from the sample.

2.3.5. TBARS determination

The fillets were homogenised with 1.5% KCl and the supernatant was used for the determination of TBARS, as described by Buege and Aust (1978). The samples were incubated at 100 °C for 15 min, in a medium containing trichloroacetic acid and thiobarbituric acid. After incubation, butyl alcohol was used to extract the reaction product that was determined at 535 nm.

2.3.6. Fatty acid profile

The fatty acid composition of the fish fillets and of the oil, used in the frying process, was determined by gas chromatography. The oil samples were analysed before frying. The fat was saponified in methanolic KOH solution and then esterified in methanolic H_2SO_4 solution (Hartman & Lago, 1973). The fatty acid methyl esters (FAME) were analysed using an Agilent Technologies gas chromatograph (HP 6890) fitted with a capillary column DB-23 (50% cyanopropyl-methylpolysiloxane, 60 m × 0.25 mm × 0.25 μm) with flame ionisation detection. The injection and detector temperatures were set at 250 °C and the carrier gas was nitrogen (0.6 ml min^{-1}). After injection (1 μl, split ratio 50:1) the column temperature was held at 120 °C for 5 min, then increased to 240 °C at 4 °C min^{-1} and held at this temperature for 10 min. The standard fatty acid methyl esters were run under the same conditions and the subsequent retention times were used to identify the fatty acids. The fatty acids were expressed as percentages of the total fatty acid content in the standard.

2.4. Statistical analyses

The effect of the heat treatment on the proximate and fatty acid composition and on the lipid oxidation parameters, was analysed by one-way analysis of variance (ANOVA). Post hoc analysis was carried out using Tukey's test. Differences were considered to be significant when $p < 0.05$. Data were analysed using the Statistica 6.0 software package.

3. Results and discussion

3.1. Proximate composition

The changes in moisture, ash, protein, and fat content of samples after cooking processes are shown in Table 1. The proximate composition of raw fillets is similar to that observed by Lazzari et al. (2006) for silver catfish juveniles (*Rhamdia quelen*).

The moisture content of the fish fillets ranged from 45% to 80%, decreasing after cooking, except for the boiled fillets (Table 1). The ash content increased after cooking, except for the boiled fillets, the protein content increased after cooking in all evaluated methods and fat content increased only in fried fillets (Table 1). The decrease in the moisture content has been described as the most prominent change that makes the protein, fat and ash contents increase significantly in cooked fish fillets (García-Arias, Pontes, García-Linares, García-Fernández, & Sánchez-Muniz, 2003). Accordingly, the increase in ash, protein and fat content found in cooked silver catfish fillets is explained by the reduction in moisture (Table 1).

When the data were expressed on a dry matter basis, only the fat content of fried silver catfish was significantly higher (twofold) than that of the raw fillets (data not shown). This indicates that the increase in fat content of the fried fish fillets is also related to oil absorption during the cooking process. Similar results were found for sardines fried in sunflower oil (Candela, Astiararán, & Bello, 1998). Fat increase can be due to the oil penetration on the food after water is partially lost by evaporation (Saguy & Dana, 2003).

During the oven-baking, silver catfish fillets lost water with a consequent increase in protein, fat and ash content. However, dehydration was lower than during frying. These changes were similar to those found by Gokoglu, Yerlikaya, and Cengiz (2004) in rainbow trout and García-Arias et al. (2003) in sardines. Grilling produced higher water losses than oven-baking, but lower than frying. These modifications appear to be related to the rate of change in food

Table 1
Proximate composition of raw and cooked fish fillets

Cooking methods	Moisture	Ash	Protein	Fat
Raw	79.6 ± 0.82^{a}	1.08 ± 0.02^{d}	15.5 ± 0.19^{d}	2.51 ± 0.45^{b}
Boiled	$74.9 \pm 0.17^{a,b}$	0.95 ± 0.04^{d}	20.1 ± 0.27^{c}	2.45 ± 0.17^{b}
Oven-baked	$70.2 \pm 0.46^{b,c}$	1.54 ± 0.04^{c}	$23.0 \pm 0.20^{b,c}$	3.64 ± 0.41^{b}
Microwave-baked	71.4 ± 0.29^{b}	1.58 ± 0.12^{c}	21.9 ± 0.51^{c}	3.37 ± 0.54^{b}
Grilled	64.9 ± 1.01^{c}	$1.97 \pm 0.07^{b,c}$	25.7 ± 0.92^{b}	3.79 ± 0.39^{b}
Fried in soybean oil	45.4 ± 1.44^{d}	2.47 ± 0.10^{a}	33.4 ± 0.58^{a}	14.0 ± 0.45^{a}
Fried in canola oil	47.0 ± 1.50^{d}	$2.41 \pm 0.08^{a,b}$	32.05 ± 1.21^{a}	13.0 ± 0.42^{a}
Fried in hydrogenated vegetable oil	46.9 ± 2.30^{d}	2.50 ± 0.14^{a}	32.2 ± 0.30^{a}	14.1 ± 1.13^{a}

Results are means ± standard error ($n = 3$). Means within the same column that have no common letters are significantly different ($p < 0.05$).

temperature (quicker in frying), and the process temperature (higher in grilling than in oven-baking). Microwave-oven cooking induced changes similar to those observed in conventional oven-baked fillets.

3.2. Free fatty acid (FFA)

To consider the complexity of the lipid oxidation process, both the primary and secondary oxidation products have been assessed. FFA content of the fillets was significantly reduced by all the cooking conditions evaluated (Fig. 1). The loss of volatile FFA probably occurred during heating, leading to a decreased FFA content. Alternatively, the higher FFA content in raw samples when compared to cooked samples could also be explained by the deactivation of enzymes, due to the heating process. This would prevent the release of free fatty acids due to lipase activity in the cooked samples. These results are in agreement with those of Al-Saghir, Thurner, Wagner, Frisch, and Luf (2004), who observed a decrease of FFA in Salmon fillets, steamed or pan-fried, either with or without different types of oil. Chantachum, Benjakul, and Sriwirat (2000) also observed a lower FFA content in oil prepared from tuna heads, by heating at 95 °C, when compared to the raw oil.

We found the lowest FFA values in the fried samples. This can be explained by dilution in the bath oil or FFA volatilisation. Aro et al. (2000) reported that the free fatty acid content in Baltic herring decreased with frying, by dilution in rapeseed oil.

3.3. Conjugated dienes

The CD value decreased for all fried samples but remained constant in the other cooked samples (Fig. 2). During the oxidation of PUFAs containing methylene substituted dienes and polyenes, there is a shift in the position of the double bond due to isomerisation and conjugate bond formation (conjugated dienes) (Zuta et al., 2007). This is accompanied by increased UV absorption at 234 nm. It is an indicator of autooxidation and is reported to increase with uptake of oxygen and formation of peroxides, during the early stages of oxidation (Farmer, 1946). Thus, CDs are the primary oxidation products formed. The decrease of CDs in fried products probably occurred because of their decomposition into secondary oxidation products.

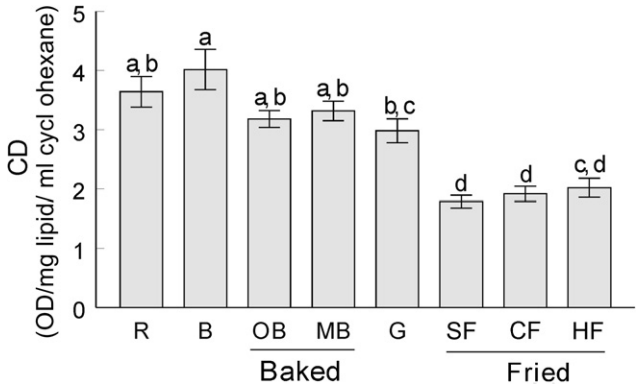

Fig. 2. Changes in conjugated diene value (CD) in silver catfish fillets submitted to different cooking methods: raw (R), boiled (B), oven-baked (OB), microwave-baked (MB), grilled (G), soybean oil-fried (SF), canola oil-fried (CF), hydrogenated vegetable oil-fried (HF). Results are means ± standard error ($n = 3$). Bars that have no common letters are significantly different ($p < 0.05$). OD, optical density.

3.4. Peroxide value

There was no difference in the peroxide value of the boiled, baked or grilled fillets when compared to the raw fillets (Fig. 3). Our results for grilled fillets are in accordance with those of Oshima, Shozen, Ushio, and Koizumi (1996) who did not observe changes in the peroxide value of grilled anchovies.

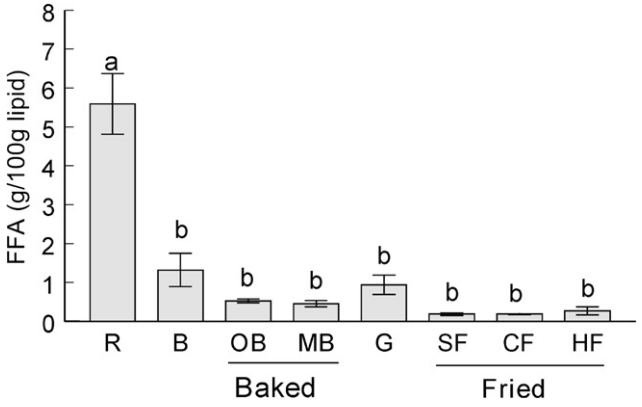

Fig. 1. Changes in free fatty acid (FFA) content in silver catfish fillets, submitted to different cooking methods: raw (R), boiled (B), oven-baked (OB), microwave-baked (MB), grilled (G), soybean oil-fried (SF), canola oil-fried (CF), hydrogenated vegetable oil-fried (HF). Results are means ± standard error ($n = 3$). Bars that have no common letters are significantly different ($p < 0.05$).

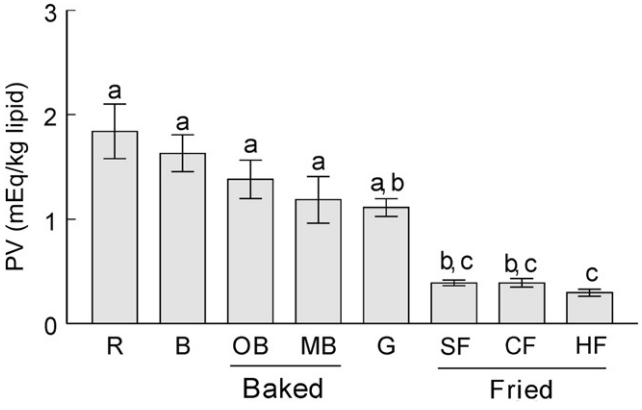

Fig. 3. Changes in peroxide value (PV) in silver catfish fillets submitted to different cooking methods: raw (R), boiled (B), oven-baked (OB), microwave-baked (MB), grilled (G), soybean oil-fried (SF), canola oil-fried (CF), hydrogenated vegetable oil-fried (HF). Results are means ± standard error ($n = 3$). Bars that have no common letters are significantly different ($p < 0.05$).

All the fried silver catfish fillets had a significant decrease in the peroxide value when compared to the raw, boiled and baked samples (Fig. 3). Although there is a report of unchanged peroxides after the deep-frying of sardines (Sanchéz-Muniz, Viejo, & Medina, 1992), other authors observed an important decrease in the peroxide value after the frying of Baltic herring fillets (Aro et al., 2000). At high temperatures, the initial hydroperoxides formed exist only transiently and will be rapidly decomposed into various volatile and non-volatile products (Frankel, 1998; Saguy & Dana, 2003). This could explain the decrease in peroxides during the frying process.

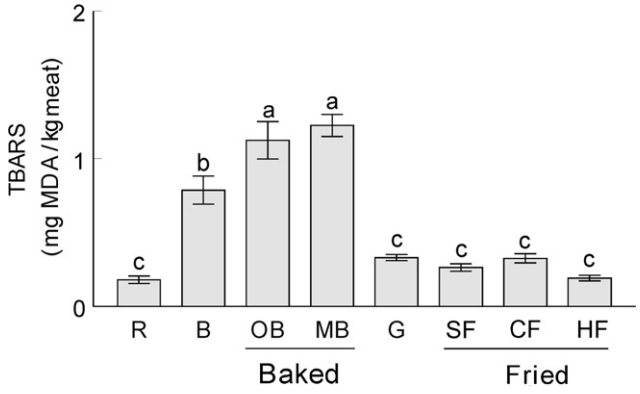

Fig. 4. Changes in TBARS value in silver catfish fillets submitted to different cooking methods: raw (R), boiled (B), oven-baked (OB), microwave-baked (MB), grilled (G), soybean oil-fried (SF), canola oil-fried (CF), hydrogenated vegetable oil-fried (HF). Results are means ± standard error ($n = 3$). Bars that have no common letters are significantly different ($p < 0.05$). MDA, malonaldehyde.

3.5. TBARS

Secondary lipid oxidation was studied by the TBARS value, which is an index of malonaldehyde (MDA) concentration. MDA is one of the main end-products of lipid oxidation. The formation of TBARS is shown in Fig. 4. A significant increase in the TBARS value was observed in boiled and baked samples, with higher values in the samples baked in microwave and conventional ovens. We did not find studies evaluating the effect of boiling or baking on the TBARS value of fish fillets. The increase in the TBARS values after boiling and baking probably occurred due to the high temperature that promoted lipid peroxidation, increasing malonaldehyde levels. In contrast, no significant differences were observed in the TBARS value of grilled and fried samples, when compared with the raw

Table 2
Fatty acid composition (% of total fatty acids) of silver catfish fish fillets submitted to different cooking methods

Fatty acid	Raw	Boiled	Oven-baked	Microwave-baked	Grilled	Fried in soybean oil	Fried in canola oil	Fried in hydrogenated vegetable oil
C14:0	1.34 ± 0.05^{a}	1.27 ± 0.09^{a}	1.37 ± 0.02^{a}	1.38 ± 0.15^{a}	1.22 ± 0.03^{a}	0.16 ± 0.01^{b}	0.23 ± 0.02^{b}	0.35 ± 0.03^{b}
C16:0	24.6 ± 0.67^{a}	25.0 ± 0.32^{a}	24.2 ± 0.24^{a}	24.5 ± 0.45^{a}	23.5 ± 0.40^{a}	12.3 ± 0.07^{c}	9.21 ± 0.46^{d}	20.6 ± 0.66^{b}
C18:0	8.38 ± 0.11^{b}	8.67 ± 0.30^{b}	8.25 ± 0.21^{b}	8.55 ± 0.25^{b}	8.02 ± 0.35^{b}	4.27 ± 0.03^{c}	4.54 ± 0.32^{c}	18.3 ± 0.36^{a}
C20:0	n.d.	0.43 ± 0.03^{b}	0.44 ± 0.01^{b}	0.44 ± 0.01^{b}	0.45 ± 0.01^{b}	0.47 ± 0.02^{b}	0.90 ± 0.02^{a}	0.87 ± 0.03^{a}
C22:0	n.d.	n.d.	0.10 ± 0.06^{c}	0.10 ± 0.07^{c}	0.14 ± 0.07^{c}	0.44 ± 0.01^{b}	0.41 ± 0.01^{b}	0.78 ± 0.03^{a}
C24:0	$0.66 \pm 0.05^{a,b}$	0.77 ± 0.06^{a}	$0.59 \pm 0.06^{a,b,c}$	$0.62 \pm 0.08^{a,b,c}$	$0.62 \pm 0.03^{a,b,c}$	0.27 ± 0.02^{d}	$0.39 \pm 0.02^{c,d}$	$0.45 \pm 0.01^{b,c,d}$
∑SFA	34.9 ± 0.58^{b}	36.1 ± 0.47^{b}	35.0 ± 0.49^{b}	35.6 ± 0.57^{b}	33.9 ± 0.76^{b}	18.0 ± 0.16^{c}	15.7 ± 0.60^{c}	41.4 ± 1.01^{a}
C14:1*n*−5	n.d.	n.d.	0.26 ± 0.02^{a}	0.29 ± 0.05^{a}	n.d.	n.d.	n.d.	n.d.
C16:1*n*−7c	5.39 ± 0.34^{a}	5.50 ± 0.53^{a}	5.48 ± 0.06^{a}	6.09 ± 0.94^{a}	5.07 ± 0.12^{a}	0.39 ± 0.04^{b}	0.82 ± 0.10^{b}	0.84 ± 0.14^{b}
C18:1*n*−9c	29.8 ± 0.87^{b}	27.5 ± 0.96^{b}	29.2 ± 0.46^{b}	29.9 ± 1.27^{b}	28.9 ± 0.31^{b}	$26.0 \pm 0.09^{b,c}$	72.5 ± 0.76^{a}	21.5 ± 2.58^{c}
C20:1*n*−9	0.95 ± 0.02^{b}	0.96 ± 0.002^{b}	1.03 ± 0.04^{b}	1.04 ± 0.01^{b}	0.93 ± 0.07^{b}	0.33 ± 0.01^{c}	1.42 ± 0.05^{a}	0.57 ± 0.10^{c}
C22:1*n*−9	n.d.	0.46 ± 0.03^{a}	0.33 ± 0.07^{a}	0.35 ± 0.06^{a}	0.34 ± 0.01^{a}	$0.06 \pm 0.01^{b,c}$	$0.10 \pm 0.01^{b,c}$	0.11 ± 0.01^{b}
∑MUFA	34.2 ± 0.98^{b}	34.5 ± 1.42^{b}	36.3 ± 0.52^{b}	37.6 ± 2.20^{b}	35.2 ± 0.30^{b}	26.9 ± 0.15^{c}	74.8 ± 0.64^{a}	23.0 ± 2.34^{c}
C18:2*n*−6t	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14.18 ± 0.20
C18:2*n*−6c	19.2 ± 0.56^{b}	17.6 ± 0.84^{b}	19.0 ± 0.81^{b}	17.2 ± 1.18^{b}	20.9 ± 1.07^{b}	48.7 ± 0.16^{a}	0.21 ± 0.02^{c}	17.9 ± 0.87^{b}
C18:3*n*−3	1.41 ± 0.05^{c}	1.26 ± 0.06^{c}	1.54 ± 0.06^{c}	1.38 ± 0.10^{c}	1.60 ± 0.12^{c}	4.88 ± 0.07^{b}	7.09 ± 0.12^{a}	0.82 ± 0.15^{c}
C20:4*n*−6	3.25 ± 0.31^{a}	4.16 ± 0.34^{a}	3.18 ± 0.29^{a}	3.23 ± 0.43^{a}	3.20 ± 0.14^{a}	0.61 ± 0.01^{b}	0.87 ± 0.07^{b}	1.04 ± 0.11^{b}
C20:5*n*−3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10 ± 0.03	n.d.
C22:5*n*−3	1.24 ± 0.17^{a}	1.47 ± 0.22^{a}	1.15 ± 0.09^{a}	1.17 ± 0.16^{a}	1.18 ± 0.06^{a}	0.18 ± 0.01^{b}	0.25 ± 0.02^{b}	0.29 ± 0.03^{b}
C22:6*n*−3	3.90 ± 0.40^{a}	4.89 ± 0.48^{a}	3.81 ± 0.34^{a}	3.76 ± 0.90^{a}	4.07 ± 0.23^{a}	0.73 ± 0.01^{b}	1.02 ± 0.10^{b}	1.37 ± 0.16^{b}
∑PUFA	$29.0 \pm 1.10^{b,c}$	$29.4 \pm 1.39^{b,c}$	$28.7 \pm 0.51^{b,c}$	26.8 ± 2.56^{c}	$30.9 \pm 0.85^{b,c}$	55.1 ± 0.30^{a}	9.52 ± 0.05^{d}	35.6 ± 1.34^{b}
∑*n*−3	6.51 ± 0.50^{a}	7.55 ± 0.63^{a}	6.45 ± 0.37^{a}	6.25 ± 0.97^{a}	6.78 ± 0.18^{a}	5.79 ± 0.07^{a}	8.34 ± 0.01^{a}	2.48 ± 0.31^{b}
∑*n*−6	22.3 ± 0.71^{b}	21.6 ± 0.91^{b}	22.0 ± 0.61^{b}	20.3 ± 1.57^{b}	23.9 ± 0.98^{b}	49.3 ± 0.23^{a}	1.08 ± 0.09^{c}	18.9 ± 0.95^{b}
n−3/*n*−6	0.29 ± 0.02^{b}	0.35 ± 0.02^{b}	0.29 ± 0.02^{b}	0.30 ± 0.02^{b}	0.28 ± 0.02^{b}	0.12 ± 0.01^{b}	7.81 ± 0.59^{a}	0.13 ± 0.01^{b}
UFA/SFA	$1.81 \pm 0.08^{c,d}$	$1.77 \pm 0.03^{c,d}$	$1.86 \pm 0.04^{c,d}$	$1.81 \pm 0.04^{c,d}$	1.95 ± 0.07^{c}	4.55 ± 0.05^{b}	5.39 ± 0.25^{a}	1.42 ± 0.06^{d}

Values are means ± standard error ($n = 3$). Means within the same row that have no common letters differ significantly ($p < 0.05$). SFA, saturated fatty acid; PUFA, polyunsaturated fatty acid; MUFA, monounsaturated fatty acid and n.d., not detected.

fillets (Fig. 4). In the fried and grilled fillets, the MDA eventually formed could be lost either by dissolution in the frying oil or due to formation of adducts with proteins.

According to Al-Kahtani et al. (1996), meat products can be considered in a good conservation state, concerning oxidative changes, when they have less than 3 mg MDA/kg. Hence, all samples evaluated were suitable for consumption.

3.6. Changes in fatty acid composition

The profile of the most important fatty acids of the silver catfish fillets are shown in Table 2. The most abundant fatty acids found in raw silver catfish fillets were oleic acid (C18:1*n*−9c), linoleic acid (C18:2*n*−6c) and palmitic acid (C16:0). These findings are in agreement with those obtained by Shirai, Suzuki, Tokairin, Ehara, and Wada (2002) for Japanese and Thai catfish. Raw silver catfish fillets also showed considerable amounts of palmitoleic acid (C16:1*n*−7c), estearic acid (C18:0), DHA (C22:6*n*−3) and arachidonic acid (C20:4*n*−6). However, silver catfish had low levels of the *n*−3 PUFA linolenic acid (C18:3*n*−3) and DPA (C22:5*n*−3) and no detectable levels of EPA (C20:5*n*−3). The *n*−3/*n*−6 ratio (0.3) of silver catfish is low when compared to that of Japanese catfish (∼1), but similar to that of Thai catfish (∼0.2) (Shirai et al., 2002).

Boiling, baking or grilling marginally affected the silver catfish fillets fatty acid content. Some fatty acids that were not detected in raw fillets were found at low levels after these heating treatments (C14:1*n*−5, C20:0, C22:0, and C22:1*n*−9). The minimal changes observed must be a consequence of the water loss produced by these processes. Conversely, fried silver catfish fillets showed great changes in the fatty acid profile when compared to raw samples, probably due to oil absorption during the frying process. In agreement with García-Arias et al. (2003), the changes were not homogeneous for the different fatty acids because some fatty acids decreased, while others increased. The changes observed were dependent on the composition of the frying oil.

As an important nutritional index of fatty acid alteration during cooking, *n*−3/*n*−6 ratio showed an interesting increase in silver catfish fillets fried in canola oil (Table 2). The UFA/SFA ratio was significantly different among the fillets which were fried in the three types of oil. The silver catfish fillets which were fried in the vegetable hydrogenated oil had lower UFA/SFA ratio than the grilled fillets. This was expected, due to the absorption of the saturated fatty acids from vegetable hydrogenated oil and is in agreement with the lower UFA/SFA ratio of this oil, when compared to the others (Table 3). The silver catfish fillets which were fried in canola and soybean oil had an increase in the UFA/SFA, ratio when compared to all other samples. This finding can be attributed to the high content of mono and polyunsaturated fatty acids in canola and soybean oil, respectively (Table 3; Milinsk, Padre, Hayashi, Souza, & Matsushita, 2003).

Table 3
Fatty acid composition (% of total fatty acid) of oil used in the frying process

Fatty acid	Soybean oil	Canola oil	Hydrogenated vegetable oil
C14:0	n.d.	n.d.	0.30 ± 0.01
C16:0	11.5 ± 0.04	4.75 ± 0.02	15.4 ± 0.25
C18:0	3.77 ± 0.01	2.81 ± 0.05	10.2 ± 0.27
C20:0	0.45 ± 0.01	0.75 ± 0.01	0.45 ± 0.01
C22:0	0.58 ± 0.01	0.34 ± 0.01	0.40 ± 0.01
C24:0	0.21 ± 0.01	n.d.	0.15 ± 0.01
∑SFA	16.5 ± 0.01	8.65 ± 0.02	26.9 ± 0.09
C14:1*n*−5	n.d.	n.d.	n.d.
C16:1*n*−7c	n.d.	n.d.	0.17 ± 0.02
C18:1*n*−9t	n.d.	n.d.	19.7 ± 0.35
C18:1*n*−9c	26.2 ± 0.05	66.6 ± 0.05	25.9 ± 0.63
C20:1*n*−9	0.26 ± 0.01	1.23 ± 0.01	0.28 ± 0.01
C22:1*n*−9	n.d.	n.d.	n.d.
∑MUFA	26.5 ± 0.03	67.9 ± 0.03	46.0 ± 0.25
C18:2*n*−6t	n.d.	n.d.	7.44 ± 0.20
C18:2*n*−6c	52.0 ± 0.02	18.3 ± 0.05	16.0 ± 0.18
C18:3*n*−3	5.07 ± 0.05	5.22 ± 0.01	0.13 ± 0.01
C20:4*n*−6	n.d.	n.d.	n.d.
C20:5*n*−3	n.d.	n.d.	n.d.
C22:5*n*−3	n.d.	n.d.	n.d.
C22:6*n*−3	n.d.	n.d.	n.d.
∑PUFA	57.1 ± 0.04	23.5 ± 0.03	23.5 ± 0.07
∑*n*−3	5.07 ± 0.05	5.22 ± 0.01	0.13 ± 0.01
∑*n*−6	52.0 ± 0.02	18.3 ± 0.05	16.0 ± 0.20
n−3/*n*−6	0.26 ± 0.02	0.29 ± 0.01	0.008 ± 0.01
UFA/SFA	5.07 ± 0.07	10.6 ± 0.04	2.58 ± 0.02

Values are means ± standard error ($n = 3$).

EPA, which is one of the most important fatty acids in fish lipids, was not found in raw silver catfish fillets. However, it was found in fillets fried in canola oil. DHA and DPA levels were significantly reduced during frying. This reduction is in agreement with Candela et al. (1998), who observed this loss in mackerel and sardines fried in sunflower oil. It can be explained by the oil absorption during frying. The oils used in the frying process had no DHA or DPA (Table 3). Hence, oil absorption would reduce the content of these fatty acids when compared with the others.

The samples fried in canola oil had a higher MUFA content and a lower PUFA content than the raw fillets. The fillets fried in soybean oil had the opposite behaviour. The changes in total MUFA and PUFA were attributed mainly to the frying oil used, as can be observed by the fatty acid composition of these oils (Table 3).

The use of hydrogenated vegetable oil, which initially contained approximately 27% of trans fatty acids (TFA, Table 3), increased the TFA content in the fried samples when compared with the raw fish fillets which had no TFA. The consumption of TFA is very worrying, because they can cause a higher risk of coronary disease, sudden death and possibly diabetes mellitus (Mozaffarian, 2006).

4. Conclusions

All of the cooking methods evaluated changed proximate composition, oxidation parameters and fatty acid profile of the silver catfish fillets. Changes in proximate composition were more prominent in fried fillets. Only boiled and baked fillets had increased levels of TBARS, indicating oxidative changes, but they did not reach threshold levels for preventing human consumption. Fatty acid profile was marginally affected by boiling, baking and grilling, but was greatly affected by deep-frying due to fat absorption. Grilling and canola oil-frying appeared to be the best cooking methods concerning oxidative stability and the fatty acid profile. The increase in $n-3/n-6$ ratio produced by frying in canola oil enhanced the nutritional value of silver catfish.

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