Fatty acids, cholesterol, oxidative rancidity, and color of irradiated shrimp

Ácidos graxos, colesterol, rancidez oxidativa e cor de camarões irradiados

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Abstract

The effect of gamma irradiation (0, 2, 4, and 6 kGy doses) applied to frozen and packed headed shrimp on the fatty acid profile, cholesterol content, and lipid and color stability was evaluated. Myristic acid was higher in shrimp irradiated with 4 and 6 kGy and palmitic acid was higher in samples irradiated with 2 and 6 kGy compared to non-irradiated samples. Stearic and behenic acids were lower in shrimp irradiated with 6 kGy compared to non-irradiated shrimp. With regard to non-irradiated shrimp, palmitoleic, oleic, and linoleic acids and total monounsaturated fatty acids were higher in shrimp irradiated with 6 kGy. Saturated fatty acid and cholesterol contents in irradiated samples were not different from those in non-irradiated shrimp. Lipid oxidation was higher in samples irradiated with 2, 4, and 6 kGy. Redness and yellowness of cooked shrimp were higher in samples irradiated with 6 kGy than in those in non-irradiated samples. The application of irradiation in doses up to 6 kGy on frozen and packed headed shrimp does not affect negatively the fatty acid profile, cholesterol content, and lipid and color stability.

Keywords: irradiation; fatty acids; TBARS, L*, a*, b*.

1 Introduction

Shrimp farming is the sector of the aquaculture that shows the highest growing potential worldwide. Brazilian cultured shrimp production is an important economical activity in the northeast region of the country. Currently, Penaeus vannamei, the most intensively exploited species in the region, has reached high economic value at the local and external market levels (BARBIERI JÚNIOR; OSTRENSKY NETO, 2002; CARVALHO et al., 2005).

Shrimp is a rich source of protein, and its lipids are highly unsaturated compared to those of red meat. The most important unsaturated fatty acids in shrimp are eicosapentaeenoic (20:5, EPA) and docosahexaenoic (22:6, DHA), which are also considered as essential fatty acids. Moreover, shrimp is a good source of minerals such as calcium, and it is also considered a high cholesterol food (MOURA; TENUTA-FILHO, 2002).

Foods from animal origin are the main sources of cholesterol in the human diet. Cholesterol is a stable compound that in the food is closely associated with others lipids. However, lipid oxidation can lead to oxidation of cholesterol (NAM et al., 2001).

Irradiation of lipids and fats may produce carbonyl groups and other oxidation products, such as peroxides. It is generally assumed that irradiation in the presence of oxygen increases oxidative changes. Rancidity is a sensory effect markedly perceptible when lipids are irradiated in the presence of oxygen (SANTOS et al., 2003; VENUGOPAL; DOKE; THOMAS, 1999).

Color is an important quality attribute that influences consumer acceptance of meat and fishery products. Free radicals generated by irradiation can react with myoglobin or carotenoid pigments leading to discoloration of several food products (LAWRIE, 2005).

Resumo

Foi estudado o efeito da radiação gama (doses de 0, 2, 4 e 6 kGy) em caudas de camarão congeladas e embaladas, sobre os conteúdos de ácidos graxos e colesterol, bem como sobre a estabilidade dos lipídios e da cor. Com relação ao camarão não irradiado, os ácidos mirístico e palmitico apresentaram maiores valores nos camarões irradiados com 4 e 6 kGy e com 2 e 6 kGy, respectivamente. Os ácidos estéarico e behénico foram menores nas amostras irradiadas com 6 kGy em relação às não irradiadas. Os ácidos palmitoleico, oleico, linoleico e o total de ácidos graxos monounsaturados foram maiores nos camarões irradiados com 6 kGy do que naqueles não irradiados. Para o total de ácidos graxos saturados e conteúdo de colesterol, as amostras irradiadas não diferiram daquelas não irradiadas. A oxidação lipídica aumentou com a irradiação. Os componentes de cor a* e b* do camarão cozido foram maiores com 6 kGy. A irradiação em doses de até 6 kGy não afetou negativamente o perfil de ácidos graxos, o nível de colesterol e a estabilidade dos lipídios e da cor das caudas de camarões.

Palavras-chave: irradiação; ácidos graxos; TBARS, L*, a*, b*.
Although irradiation is considered an effective technology in food preservation, it can cause significant changes in product quality, such as lipid oxidation and other chemical changes. Since fish lipids are more unsaturated as compared to those of red meat, their sensitivity to irradiation is one of the parameters that has been considered to optimize radiation doses used for fish preservation (LAKSHMANAN et al., 1999).

Thus, the objective of this study was to verify the effect of gamma irradiation applied on frozen and packed headed shrimp on fatty acid and cholesterol contents, as well as on lipid and color stability.

2 Materials and methods

2.1 Experimental design and preparation of shrimp samples

In this study a complete randomized design (4 × 5) with four irradiation doses (0, 2, 4, and 6 kGy) and five replicates was used.

Fresh medium size (80 to 100 tails.kg⁻¹) headed shrimp, Panaxus vannamei, was obtained from a local industry operating in accordance with the Brazilian Federal Inspection Service (BRASIL, 2001) and transported to the laboratory in a thermal container (shrimp and ice at the rate of 1:1). After separating from ice, the shrimp was divided into 300 g portions, packed in polyethylene (0.15 mm thick) bags and added of 200 mL of water. The bags were then sealed, packed in cardboard boxes (14.5 × 11.0 × 4.5 cm, internally lined with polyethylene film) and frozen at −30 °C for 12 hours. Those packages were considered the Experimental Unit (EU) for the study.

Five frozen EU were then packed in four cardboard master boxes (18.0 × 27.0 × 36.0 cm) and stored at −20 °C until irradiation. Each box was then irradiated under a 60 Cobalt source with doses of 0, 2, 4, or 6 kGy at a dose rate of 1500 Gy/hour.

EUs were then analyzed for fatty acid and cholesterol concentrations, lipid oxidation, and color stability.

2.2 Analysis of irradiated shrimp

For fatty acid composition analysis, EUs were ground into a homogenous mass using a domestic food processor. About 10 g of shrimp homogenate were freeze-dried for 24 hours. The dehydrated shrimp samples were then vacuum-packed in nylon-polyethylene bags and stored at 1 °C until preparation in the form of fatty acid methyl esters.

The fatty acids were extracted from freeze-dried shrimp and converted into methyl esters according to the procedure described by Rule et al. (2002). Chromatographic analyses were performed using a gas chromatograph (VARIAN CP 3380, Walnut Creek, USA), equipped with fused silica capillary column (100 m × 0.25 mm i.d.) and a Flame Ionization Detector (FID). Hydrogen was used as the carrier gas at a flow rate of 1.5 mL/minute. The initial temperature of the column was set at 160 °C and was increased to 240 °C at a rate of 3.5 °C/minute, and then it was held at 240 °C for an additional 10 minutes period. The detector and injection port were maintained at 250 °C.

In this study, a total of 14 fatty acids were identified in non-irradiated or irradiated headed shrimp (Table 1). The predominant fatty acids found were stearic (18:0) and palmitic (16:0). These results are in agreement with those of Perez-Velazquez et al. (2003), who also reported that these fatty acids were the most abundant in pacific white shrimp (Litopenaeus vannamei).
Table 1. Fatty acids (mean percentages) of headed shrimp (P. vannamei) measured after freezing, packaging, and irradiating (60Co) with 0, 2, 4, or 6 kGy doses11.

| Fatty acids (%) | Dose (kGy) |
|----------------|------------|
|                | 0          | 2          | 4          | 6          |
| C14:0-11       | 0.84 ± 0.19| 1.20 ± 0.41| 1.52 ± 0.26| 1.35 ± 0.16|
| C16:0          | 23.24 ± 0.52| 24.44 ± 0.56| 21.59 ± 0.95| 24.70 ± 0.91|
| C18:010        | 41.32 ± 1.57| 42.30 ± 1.57| 40.89 ± 1.39| 37.72 ± 1.51|
| C20:0          | 0.60 ± 0.03| 0.62 ± 0.01| 0.65 ± 0.06| 0.58 ± 0.02|
| C22:011        | 0.13 ± 0.06| 0.07 ± 0.02| 0.07 ± 0.02| 0.03 ± 0.01|
| C16:110        | 0.80 ± 0.11| 0.59 ± 0.07| 0.72 ± 0.13| 1.12 ± 0.14|
| C18:110        | 8.51 ± 0.55| 6.75 ± 1.39| 7.90 ± 1.45| 12.15 ± 1.73|
| C20:1          | 0.26 ± 0.03| 0.28 ± 0.02| 0.25 ± 0.05| 0.30 ± 0.09|
| C22:110        | 0.10 ± 0.04| 0.14 ± 0.01| 0.14 ± 0.02| 0.10 ± 0.04|
| C18:210        | 5.46 ± 0.35| 4.79 ± 0.40| 4.23 ± 0.91| 6.95 ± 1.48|
| C18:310        | 0.32 ± 0.01| 0.32 ± 0.02| 0.27 ± 0.05| 0.26 ± 0.04|
| C20:4          | 1.61 ± 0.17| 1.54 ± 0.09| 1.37 ± 0.31| 1.68 ± 0.40|
| C20:5          | 4.86 ± 0.56| 4.56 ± 0.28| 4.22 ± 1.05| 4.99 ± 1.32|
| C22:6          | 3.07 ± 0.03| 3.02 ± 0.49| 2.60 ± 0.59| 2.69 ± 0.63|

11Mean values with different letters within a row are significantly different (p < 0.05) by SNK test, n = 5; 12Quadratic effect (y = 0.82 + 0.29x – 0.03x^2; R^2 = 0.49), being y = myristic acid concentration; x = irradiation dose; R^2 = determination coefficient; 13Quadratic effect (y = 41.35 + 0.95x – 0.26x^2; R^2 = 0.62); 14Linear effect (y = 0.11 – 0.01x; R^2 = 0.45); 15Quadratic effect (y = 0.80 – 0.17x + 0.04x^2; R^2 = 0.78); 16Quadratic effect (y = 8.51 – 1.65x + 0.37x^2; R^2 = 0.73); 17Quadratic effect (y = 0.10 + 0.03x – 0.004x^2; R^2 = 0.30); 18Quadratic effect (y = 5.61 – 1.07x + 0.21x^2; R^2 = 0.54); 19Linear effect (y = 0.33 – 0.01x; R^2 = 0.40).

Myristic acid (14:0) was higher (p < 0.05) in headed shrimp irradiated with 4 and 6 kGy doses compared to non-irradiated shrimp. Palmitic (16:0) acid was higher (p < 0.05) in samples irradiated with 2 and 6 kGy doses than those in non-irradiated. Sfa values in shrimp samples irradiated with 6 kGy (Table 1).

Similar observations have been reported by Lakshmanan et al. (1999), who observed higher myristic and palmitic acids values and lower stearic acid values with higher irradiation doses. Stearic acid (18:0) showed lower values in shrimp samples irradiated with 6 kGy (Table 1).

Protein: 19.26 g/100 g, Lipids: 2.05 g/100 g, Moisture: 78.68 g/100 g, Ash: 1.15 g/100 g, Calcium: 0.21 g/100 g, Phosphorus: 1.56 g/100 g, Iron: 0.21 g/100 g, Total saturated Fatty Acid (SFA) in irradiated shrimp are in agreement with those of Alfaia et al. (2007), who did not observe significant changes in these fatty acids in irradiated frozen lamb meat.

Moreover, according to the regression analysis, palmitic (16:0), arachidic (20:0), eicosenoic (20:1), arachidonic (20:4), EPA (20:5), and DHA (22:6) acids were not significantly (p > 0.05) affected by irradiation of frozen and headed shrimp. However, behenic (22:0) and linolenic (18:3) acids were affected (p < 0.05) by irradiation in the form of a linear effect according to equations 4 and 9, respectively, as shown in the footnotes of Table 1.

Myristic (14:0), palmitoleic (C16:1), stearic (18:0), oleic (18:1), linoleic (C18:2), and erucic (22:1) acids were also affected (p < 0.05) by irradiation as a quadratic effect according to equations 2, 3, 5, 6, 7, and 8, respectively (footnotes, Table 1). Thus, myristic (14:0), stearic (18:0) and erucic (22:1) acids showed maximum values at 4.40, 1.82, and 2.98 kGy irradiation doses, respectively. Higher dose values provided reduction in the concentrations of these fatty acids. Palmitoleic (C16:1), oleic (18:1), and linoleic (C18:2) acids showed the lowest values at the irradiation doses of 2.28, 2.19, and 2.54 kGy, respectively. Doses higher than these increase the concentration of these fatty acids (Table 1).

Total Saturated Fatty Acid (SFA) values in irradiated shrimp were not different (p > 0.05) from those in non-irradiated shrimp. According to the regression analysis, a quadratic effect (R^2 = 0.32) was observed. Thus, SFA increased with irradiation up to the dose of 1.10 kGy. Higher dose values reduced SFA content (Table 2).

SFA values are associated with the incidence of coronary heart disease due to the increase in serum total cholesterol and decrease in Low Density Lipoproteins (LDL) (SCHAEFER, 1997). Therefore, the SFA reduction observed in irradiated shrimp could be a nutritional advantage for consumers.

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Stearic acid (18:0) was the predominant SFA found in irradiated shrimp. This fatty acid is a long-chain saturated fatty acid. However, in contrast with other saturated fatty acids, stearic acid is known to have a neutral effect on blood cholesterol concentrations. In the human organism, stearic acid is rapidly converted into oleic acid that has hypocholesterolemic effects (CASTRO et al., 2004).

As compared to non-irradiated shrimp, the total Monounsaturated Fatty Acids (MUFA) value was higher in shrimp irradiated with 6 kGy. For total MUFA, regression analysis indicated a quadratic effect (R^2 = 0.77). Thus, irradiation produced maximum reduction of MUFA at a dose of 2.19 kGy. Higher dose values provided increase of MUFA in shrimps (Table 2).

These results are in agreement with Erkan and Ozden (2007), who reported a reduction of MUFA with a low irradiation dose (2.5 kGy) and with a high irradiation dose (5.0 kGy) used on sea bream (Sparus aurata).
Oleic acid (18:1) was the main MUFA present in the irradiated shrimp, and an increase in the concentration of this acid with high irradiation doses could be a nutritional advantage for consumers due to its hypocholesterolemic effect.

No effect of irradiation (p > 0.05) was found on total polyunsaturated fatty acids (PUFA) and on the PUFA/SFA ratio (Table 2). According to Kanatt, Chander and Sharma (2006), changes in PUFA content are minimized when irradiation is carried out under frozen (−20 °C) conditions.

The predominant PUFA found were linoleic, EPA, and DHA, which are omega 3 long chain PUFA. This fact was expected because seafood is considered a high source of omega 3 long chain PUFA, which are involved in the prevention of cardiovascular diseases (SIROT et al., 2008). Thus, the effect found in this study indicates that gamma irradiation could be used on frozen headed shrimp as a form of preservation because fewer alterations occurred in PUFA content.

Cholesterol values in irradiated samples were not different (p > 0.05) from those in non-irradiated shrimp (Table 2). The radiation process leads to oxidation of cholesterol. Free radicals generated by the process of lipid peroxidation co-oxidize several molecules, especially cholesterol which is in the lipid fraction and membranes of animal tissues. The production of cholesterol oxides has also been observed in shrimp that has been processed by others methods such as boiling or deep-frying (MOURA et al., 2004). However, lowering of cholesterol levels was not observed in the present study, probably due the frozen (−20 °C) condition of the samples during irradiation.

TBARS values were higher (p < 0.05) in samples irradiated with 2, 4, and 6 kGy, as compared to non-irradiated samples (Table 3). These results are also in agreement with those found by several researchers who reported an increase of TBARS values in irradiated samples as compared to that of the non-irradiated product. Color component b* (yellowness) increased in samples irradiated with the 6 kGy dose as compared to those irradiated with 0 and 2 kGy.

These results were also in agreement with those found by several researchers who reported an increase of redness and yellowness after irradiation of animal origin food (CAVA et al., 2005; KIM et al., 2004; ZHU et al., 2003). However, Lopes (2006) who evaluated the synergic effect of gamma irradiation and refrigeration on the conservation of white shrimp (L. vannamei), did not observe significant changes in color components with irradiation.

Moreover, regression analysis indicated a linear increase (R² = 0.41, p < 0.05) of components color a* and b* with irradiation (Footnote of Table 3).

### Table 2. Saturated Fatty Acid (SFA), Monounsaturated Fatty Acid (MUFA), Polyunsaturated Fatty Acid (PUFA), PUFA/SFA ratio, and cholesterol of headed shrimp (P. vannamei) measured after freezing, packaging, and irradiating (60Co) with 0, 2, 4, or 6 kGy doses

| Dose (kGy) | SFA (%) | MUFA (%) | PUFA (%) | PUFA/SFA ratio (%) | Cholesterol (mg.100g⁻¹) |
|------------|---------|----------|----------|-------------------|------------------------|
| 0          | 65.29 ± 1.25 | 9.68 ± 0.59 | 15.31 ± 0.78 | 0.23 ± 0.01 | 121.14 ± 23.74 |
| 2          | 67.44 ± 1.88 | 7.76 ± 1.39 | 14.23 ± 0.98 | 0.21 ± 0.02 | 118.05 ± 6.01 |
| 4          | 63.20 ± 1.57 | 9.01 ± 1.06 | 12.69 ± 2.85 | 0.20 ± 0.04 | 140.27 ± 15.22 |
| 6          | 63.03 ± 2.24 | 13.71 ± 1.66 | 16.56 ± 3.14 | 0.26 ± 0.06 | 112.90 ± 4.69 |

Mean values with different letters within a column are significantly different (p < 0.05) by SNK test, n = 5; 16Mean values with different letters within a column are significantly different (p < 0.05) by SNK test, n = 5; 20Quadratic effect (y = 0.16 + 0.03x – 0.004x²; R² = 0.41); 21Linear effect (y = 7.09 + 0.31x; R² = 0.41); 22Linear effect (y = 19.66 + 0.36x; R² = 0.63).

### Table 3. TBARS values and color components L*, a*, and b* of headed shrimp (P. vannamei) measured after freezing, packaging, and irradiating (60Co) with 0, 2, 4, or 6 kGy doses

| Dose (kGy) | TBARS (%) | Color component L* | Color component a* | Color component b* |
|------------|-----------|-------------------|-------------------|-------------------|
| 0          | 0.16 ± 0.02 | 71.81 ± 3.40A | 7.17 ± 0.72 | 19.89 ± 0.87 |
| 2          | 2.30 ± 0.03 | 70.60 ± 1.34 | 7.71 ± 1.00 | 20.05 ± 0.66 |
| 4          | 2.30 ± 0.03 | 70.54 ± 1.74 | 8.17 ± 0.64 | 21.11 ± 0.89 |
| 6          | 2.30 ± 0.02 | 69.68 ± 0.44 | 9.11 ± 1.27 | 21.95 ± 1.55 |

Mean values with different letters within a column are significantly different (p < 0.05) by SNK test, n = 5; 16Mean values with different letters within a column are significantly different (p < 0.05) by SNK test, n = 5; 16Quadratic effect (y = 0.16 + 0.03x – 0.004x²; R² = 0.63); 21Linear effect (y = 7.09 + 0.31x; R² = 0.41); 22Linear effect (y = 19.66 + 0.36x; R² = 0.41).
4 Conclusions

Gamma irradiation with 60Co applied to frozen and packaged headed shrimp in doses of up to 6 kGy does not compromise negatively the fatty acid composition, cholesterol content, and lipid stability of the product. Irradiation increases the redness and yellowness of the surface color of cooked shrimp, but it does not alter its lightness.

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