ELSEVIER

0308-8146(95)00139-5

Food Chemistry, Vol. 55, No. 4, pp. 379–382, 1996

0308-8146/96 $15.00+0.00

Effect of γ-irradiation and post-irradiation cooking on thiamine, riboflavin and niacin contents of grass prawns (*Penaeus monodon*)

Kun-Fen Lee & Lung-Bin Hau*

Graduate Institute of Food Science and Technology, National Taiwan University, Taipei, Taiwan, People's Republic of China

(Received 17 February 1995; accepted 22 May 1995)

To determine the nutritional changes of grass prawns during ionizing radiation processing, the effects of irradiation doses, irradiation temperatures and the combined treatment of irradiation and cooking on thiamine, riboflavin and niacin contents of grass prawns were studied. Grass prawns were irradiated with different doses at refrigerated (4°C) or frozen (−20°C) temperatures. A domestic cooking procedure then followed irradiation. Our results indicate that radiation and post-irradiation cooking result in different changes in the vitamin contents. The loss of thiamine increased with the increase of irradiation doses and temperatures. In contrast, no significant changes were observed in either riboflavin or niacin even after irradiation doses were administered up to 7 kGy at 4 or −20°C. Moreover, significant destruction of thiamine occurred and there was no change in riboflavin or niacin after post-irradiation cooking. The total loss of thiamine after the combined treatments appears to be simply the sum of the individual losses produced by the two treatments respectively. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

The grass prawn (*Penaeus monodon*) is one of the most popular seafoods consumed in Taiwan. Under subtropically ambient conditions, such fresh prawns are a highly perishable commodity. The use of γ-irradiation to reduce the microbial population and thereby extend the shelf-life of grass prawns has already been reported (Hau *et al.*, 1992). Prawns are usually cooked in boiling water before consumption. Processing conditions such as irradiation and cooking have been reported to affect the nutrient content of irradiated foods (Kilcast, 1994). A few studies have examined the effects of γ-irradiation on the water-soluble vitamin content of shrimp. Srinivas *et al.* (1974) reported that thiamine loss in dehydro-irradiated shrimp was 35.5% at 3.2 kGy, and the loss of other B vitamins was between 8 and 18%. Hau & Liew (1993) found that no significant destruction of vitamin B_6 and B_{12} occurred when the grass prawns were irradiated with 7.0 kGy at 4 or −20°C.

Post-irradiation cooking also affects the nutritional value of the irradiated foods. Kennedy & Ley (1971) evaluated the vitamin changes in cod fish fillets and reported that riboflavin was reduced 6% by irradiation, 9% by cooking and 16% after both treatments. They concluded that irradiation followed by cooking produced a total loss which was the sum of the losses produced by each treatment. On the other hand, Thayer *et al.* (1989) found that frying bacon following irradiation produced a radiation dose-related, non-additive, increase in destruction of thiamine. Jenkins *et al.* (1989) found that thiamine losses in irradiated-then-cooked pork are greater than the additive losses of each of the individual treatments. It appears that the loss of vitamins during irradiation and post-irradiation cooking differs depending on the materials used. The purpose of the present study was to determine the effects of ionizing radiation and cooking on the thiamine, riboflavin and niacin content of grass prawns. In addition, the effects of irradiation dose and temperature on these vitamins were also evaluated.

*To whom all correspondence should be addressed.

MATERIALS AND METHODS

Grass prawns

Fresh or frozen headless prawns (approximately 20 g per prawn) were purchased from a processing plant. Prawns (five each) were air packed in polyethylene pouches and stored at 4 or −20°C. The maximum storage period was 24 h.

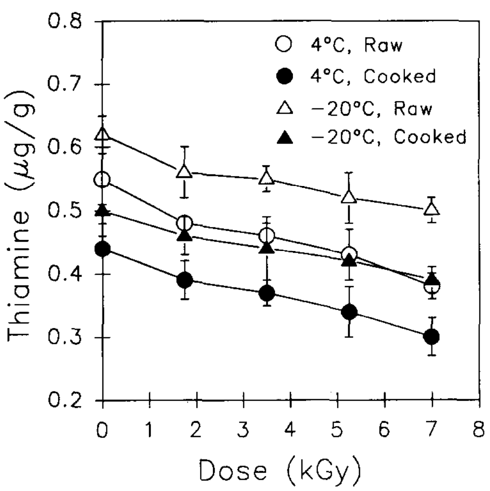

Fig. 1. Effects of irradiation and post-irradiation cooking on the thiamine content of grass prawns. Raw or cooked grass prawns were irradiated with different doses at 4 or −20°C. The thiamine contents of the irradiated samples were then determined as described in the Materials and Methods section.

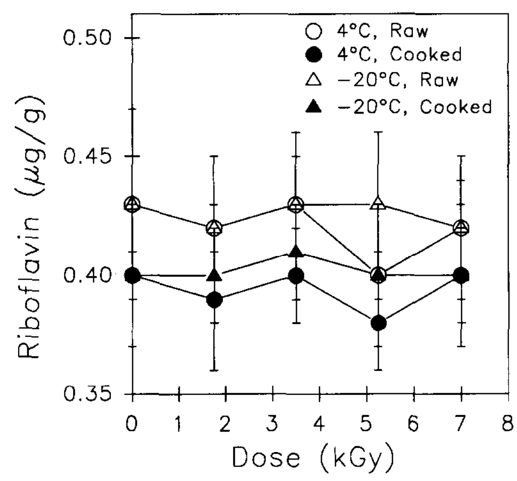

Fig. 2. Effects of irradiation and post-irradiation cooking on the riboflavin content of grass prawns. Raw or cooked grass prawns were irradiated with different doses at 4 or −20°C. The riboflavin contents of the irradiated samples were then determined as described in the Materials and Methods section.

Irradiation processing

Samples were transported to the Institute of Nuclear Energy Research and irradiated by exposure to γ-rays from a ^{60}Co source. The dose rate was 0.15 kGy/min as measured by ferrous ferric sulphate dosimetry (Jarrett, 1967). Samples were irradiated in a temperature-controlled chamber. The temperature during irradiation was measured with a thermocouple. Non-irradiated samples treated in the same way as the irradiated ones, served as the controls.

Cooking

Both irradiated and non-irradiated prawns, placed in polyethylene pouches, were immersed in boiling water for 10 min. After cooking, all drips were retained and added back to the cooked samples for vitamin analysis.

Vitamin analysis

Thiamine, riboflavin and niacin were analysed according to the methods described by the AOAC (1984). Briefly, for thiamine and riboflavin, homogenized shrimps were dispersed in 0.1 N HCl and autoclaved. Thiamine was converted to thiochrome and quantitated. Riboflavin content was determined by a fluorometric method. For niacin, homogenized shrimps were dispersed in 1.0 N H_2SO_4 and heated at 100°C for 30 min. Niacin was then determined colorimetrically after reaction with cyanogen bromide followed by sulphanilic acid.

Analysis

Data were analysed for statistical significance by analysis of variance and expressed as mean ± SD from three independent experiments (Steel & Torrie, 1984). Differences between treatments with $P < 0.05$ were considered significant.

RESULTS AND DISCUSSION

Dose effect

Radiation caused loss of thiamine in grass prawns at all doses; the loss of thiamine increased with increasing irradiation doses (Fig. 1). When irradiated at 7 kGy at 4 and −20°C, the loss of thiamine was 31 and 23%, respectively. However, no significant changes of riboflavin and niacin with irradiation doses up to 7 kGy at both 4 and −20°C were observed (Figs 2 and 3). The principal chemical change of ionizing radiation in food components is the formation of excited molecules, positive ions and electrons. The excited molecules and positive ions may split apart to generate many reactive free radicals (Taub, 1983). The B-vitamins, free or bound to specific proteins, are present primarily in the aqueous phase of the grass prawn. In the presence of water, ionizing radiation breaks water into a number of reactive species such as e_{aq}^-, OH· and H· radicals (Thomas *et al.*, 1981; Simic, 1983). In addition, water provides a good medium for movement of water-soluble vitamins and reactive species. Therefore, in the presence of water, the formation of these free radicals and reactive species are mainly responsible for the destruction of vitamins (Thayer *et al.*, 1991).

The stability of the vitamins to ionizing energy can be explained by their chemical structure and reactivity to the free radicals (Taub *et al.*, 1979; Simic, 1983). Thiamine is composed of a substituted pyrimidine and thiazole nucleus linked by a methylene bridge. The destruction of thiamine may take place in many different ways; the simplest is the split between the pyrimidine and thiazole portions of the molecule (Ziporin *et al.*,

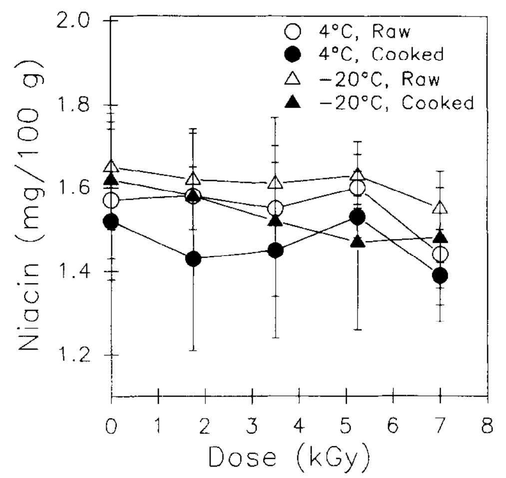

Fig. 3. Effects of irradiation and post-irradiation cooking on the niacin content of grass prawns. Raw or cooked grass prawns were irradiated with different doses at 4 or −20°C. The niacin contents of the irradiated samples were then determined as described in the Materials and Methods section.

1957). Moreover, in the presence of water, the chemical structure of thiamine is very susceptible to attack by reactive species such as: e_{aq}^-, OH· and H·. Kishore *et al.* (1978) studied the radiolysis of thiamine and suggested that thiamine was reacting with the OH· radical. Moorthy & Hayon (1977) identified a one-electron reduction intermediate from thiamine and dihydrothiamine as the end product. Therefore, in the presence of these radicals both oxidative and reductive processes may be involved in the radiolytic destruction of thiamine (Thayer *et al.*, 1991). However, because no radiolysis products of thiamine have been isolated from foods, the mechanism of destruction in food systems remains uncertain.

No significant changes of niacin and riboflavin in irradiated grass prawns were observed in this study (Figs 2 and 3). Niacin in food is, in general, very resistant to radiation. The heterocyclic pyridine ring structure of niacin is very stable and difficult to split during irradiation. Although the hydroxy radical and hydrated electron reacting with niacin give free radical intermediates in grass prawns, these intermediates can be easily oxidized with moderate oxidants, such as riboflavin and other food components (Brühlmann & Hayon, 1974; Thayer *et al.*, 1991). Therefore, the niacin group of vitamins had undergone very little damage in the presence of oxidizing agents.

Riboflavin is a strong oxidant which contains several sites susceptible to attack by reactive species such as hydrated electrons and free radicals (H·, OH·) (Fujimaki & Morita, 1968). However, riboflavin appears to be very resistant to radiation in grass prawns. Similar results were also reported by Srinivas *et al.* (1974) in dehydrated–irradiated shrimps after storage. This is not surprising since riboflavin is quite stable to chemical attack and is reversibly reduced to dihydroriboflavin by reducing agents. In addition, riboflavin is normally bound to proteins which protect the prosthetic groups from being attacked directly or indirectly by irradiation (Tobback, 1977). Kishore *et al.* (1978) found that the destruction of riboflavin in buffer system is due both to its oxidation by OH· radicals and to the glucose which protects riboflavin against radiation. Thus, the presence of the protecting groups or the relative stability in chemical structure may account for the radiation resistance of riboflavin in grass prawns.

Temperature effect

No significant difference in niacin and riboflavin as a function of temperature was found during irradiation (Figs 2 and 3). As mentioned above, these vitamins are very resistant to ionizing radiation. However, increased radiolytic stability of thiamine was observed at decreased temperature, the destruction of thiamine was significantly lowered at −20°C as compared to at 4°C (Fig. 1).

In the frozen state, the diffusion rates of radicals and the reactivity of the radical acceptors in the food constituents are drastically reduced (Diehl, 1983). In the case of frozen prawns, because of the very small quantity of 'free water' present, the mobility of free radicals would be dramatically reduced. Vitamin molecules would be much less susceptible to free radical interactions, particularly the interactions with the highly reactive ones generated through radiolysis of water. Thus, the susceptibility of vitamins to oxidative degradation in frozen prawns was decreased. In addition, chemical reactions associated with the direct effect of ionizing radiation on the vitamin molecules would also have been substantially reduced at subfreezing temperatures owing to the difference in activation energy of the reaction (Thomas *et al.*, 1981). The almost complete elimination of indirect effects and the reduction in net effects of direct action would explain the increase in thiamine losses as the temperature increases from −20 to 4°C.

Post-irradiation cooking

Since domestic cooking is expected prior to consumption of grass prawns, the destructive effects of cooking and the combined effects of ionizing radiation and cooking were evaluated.

Thermostability

In grass prawns, the loss of vitamins during the cooking process depends on the thermostability of the individual vitamin. Statistical analysis of the non-irradiated raw and cooked grass prawn samples indicated that cooking had no significant effects on the riboflavin and niacin contents in grass prawns. In contrast, the thiamine content significantly decreased upon cooking. The loss of thiamine was 20 and 19%, respectively, in refrigerated and frozen samples. These results are in good agreement with the existing information that thiamine is generally considered the least stable vitamin upon heating (Tannenbaum *et al.*, 1985).

Post-irradiation cooking effect

The combined effects of ionizing radiation and post-irradiation cooking on the vitamin contents of grass prawns were then evaluated. A significant destruction of thiamine (Fig. 1), but not of riboflavin and niacin, was observed (Figs 2 and 3). In this study, the destruction of thiamine in unirradiated samples upon heating was 20% at 4°C. Thiamine losses for raw shrimps irradiated at 1.75, 3.50, 5.25 and 7.0 kGy were 13, 16, 22 and 31%, respectively. The losses of thiamine of those samples cooked following irradiation were 29, 33, 38 and 46% for the respective doses of 1.75, 3.5, 5.25 and 7.0 kGy. Thus irradiation followed by cooking produces a total thiamine loss which is the sum of the losses produced by individual treatments. Similar trends were observed in frozen samples.

Several studies have been conducted on the effects of combined heat and radiation on the loss of vitamins, the results of which are controversial. Brooke *et al.* (1964) reported no loss of vitamins in irradiated clam meat following a heating process. Kennedy & Ley (1971), on the other hand, observed that irradiation followed by cooking produces a total loss of vitamins equal to the sum of the losses produced by each treatment. In addition, increased cooking losses of thiamine in irradiated samples was found both in bacon (Thayer *et al.*, 1989) and in pork (Jenkins *et al.*, 1989).

Our results indicate that vitamins behave differently after radiation and post-irradiation cooking. Among the vitamins studied, irradiation at doses up to 7 kGy did not have any significant effect on either riboflavin or on niacin. Since the destruction of niacin and riboflavin in the combined treatment is similar to the regular cooking process, the introduction of radiation processing would be of no consequence in this respect. Thiamine was the only vitamin which was lost significantly during irradiation and post-irradiation cooking. Thus, thiamine is the most important vitamin to be assessed in relation to a proposed radiation process of grass prawns.

REFERENCES

AOAC (1984). *Official Method of Analysis*. Association of Official Analytical Chemists Washington, DC.

Brooke, R. O., Ravesi, E. M., Gadbois, D. M. & Steinberg, M. A. (1964) Preservation of fresh unfrozen fishery products by low-level radiation. III. The effects of radiation pasteurization on amino acids and vitamins in clams. *Food Technol.*, **18**, 1060–4.

Brühlmann, U. & Hayon, E. (1974). One-electron redox reactions of water-soluble vitamins. I. Nicotinamide (vitamin B_5) and related compounds. *J. Am. Chem. Soc.*, **96**, 6169–75.

Diehl, J. F. (1983). Radiolytic effects in foods. In *Preservation of Food by Ionizing Radiation*, Vol. I, eds E. S. Josephson, & M. S. Peterson. CRC Press, Boca Raton, Florida, pp. 279–346.

Fujimaki, M. & Morita, M. (1968). Radiation chemistry of foods. I. Reaction rate constants of some foods constituents with hydrated electrons and hydroxyl radicals. *Agric. Biol. Chem.*, **32**, 574–9.

Hau, L.-B. & Liew, M. S. (1993). Effects of γ-irradiation and cooking on vitamins B_6 and B_{12} in grass prawns (*Penaeus monodon*). *Radiat. Phys. Chem.*, **42**, 297–300.

Hau, L.-B., Liew, M. S. & Yeh L. T. (1992). Preservation of grass prawns by ionizing radiation. *J. Food Prot.*, **55**, 198–202.

Jarrett, R. D., Jr (1967). Radiation dosimetry in relation to high intensity radiation sources. *Adv. Chem.*, **65**, 78–86.

Jenkins, R. K., Thayer, D. W. & Hansen, T. J. (1989). Effect of low-dose irradiation and post-irradiation cooking and storage on the thiamin content of fresh pork. *J. Food Sci.*, **54**, 1461–5.

Kennedy, T. S. & Ley, F. J. (1971). Studies on the combined effects of gamma radiation and cooking on the nutritional value of fish. *J. Sci. Food. Agric.*, **22**, 145–8.

Kilcast, D. (1994). Effect of irradiation on vitamins. *Food Chem.*, **49**, 157–64.

Kishore, K., Moorthy, P. N. & Rao, K. N. (1978). Radiation protection of vitamins in aqueous systems. *Radiat. Eff.*, **38**, 97–105.

Moorthy, P. N. & Hayon, E. (1977). One-electron redox reactions of water-soluble vitamins IV. Thiamin (vitamin B_1), biotin, and pantothenic acid. *J. Org. Chem.*, **42**, 879–85.

Simic, M. G. (1983). *Radiation Chemistry of Water-Soluble Food Components. Preservation of Food by Ionizing Radiation*, Vol. II, eds E. S. Josephson & M. S. Peterson. CRC Press, Boca Raton, Florida, pp. 1–70.

Srinivas, H., Vakil, V. K. & Sreenivasan, A. (1974). Nutritional and compositional changes in dehydro-irradiated shrimp. *J. Food Sci.*, **39**, 807–11.

Steel, R. G. D. & Torrie, J. H. (1984). Principles and procedures of statistics. In *A Biometrical Approach* (2nd edn). McGraw-Hill Book Co., New York.

Tannenbaum, S. R., Young, V. R. & Archer, M. C. (1985). Vitamins and minerals. In *Food Chemistry*, ed. O. R. Fennema. Marcel Dekker, New York, pp. 478–543.

Taub, I. A. (1983). Radiation mechanisms, irradiation parameters and product formation. In *Preservation of Food by Ionizing Radiation*, Vol. II, eds E. S. Josephson & M. S. Peterson. CRC Press, Boca Raton, Florida, pp. 125–66.

Taub, I. A., Kaprielian, R. A., Halliday, J. W., Walker, J. E., Angelini, P. & Merritt, C., Jr (1979). Factors affecting the radiolytic effects in food. *Radiat. Phys. Chem.*, **14**, 639–53.

Thayer, D. W., Fox, J. N. Jr & Lakritz, L. (1991). Effects of ionizing radiation on vitamins. In *Food Irradiation*, ed. S. Thorne. Elsevier Applied Science, London, pp. 285–325.

Thayer, D. W., Shieh, J. J., Jenkins, R. K., Phillips, J. G., Wierbicki, E. & Ackerman, S. A. (1989). Effect of gamma ray irradiation and frying on the thiamine content of bacon. *J. Food Qual.*, **12**, 115–34.

Thomas, M. H., Atwood, B. M., Wierbicki, E. & Taub, I. A. (1981). Effect of radiation and conventional processing on the thiamin content of pork. *J. Food Sci.*, **46**, 824–8.

Tobback, P. P. (1977). Radiation chemistry of vitamins. In *Radiation Chemistry of Major Food Components*, eds P. S. Elias & A. J. Cohen. Elsevier Science, New York, pp. 187–220.

Ziporin, Z. Z., Kraybill, H. F. & Thach, H. J. (1957). Vitamin content of foods exposed to ionizing radiations. *J. Nutrit.*, **63**, 201–9.