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Arsenic in the prepared edible brown alga hijiki, *Hizikia fusiforme*

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To reduce the arsenic content of the leaves and branches of an edible brown alga, hijiki *Hizikia fusiforme*, the Japanese traditional washing and soaking process before cooking was shown to be effective: about 32 to 60% of the arsenic was removed from the alga at room temperature. Increasing the amount of water in which the hijiki was soaked did not affect arsenic removal. On the other hand, arsenic content decreased linearly as the temperature used to wash and soak hijiki increased from 0 to 60 °C. In the washed and soaked hijiki, inorganic arsenic accounts for 90% of the total arsenic and dimethylated arsenic compounds 10%. **Copyright © 2001 John Wiley & Sons, Ltd.**

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INTRODUCTION

Marine products usually have high arsenic contents because marine organisms generally accumulate much more arsenic in their tissues and organs than do terrestrial organisms.[1–5] The arsenic compounds in marine organisms are classified into water-soluble and lipid-soluble compounds.[6,7] The former compounds are predominant in both animals and algae.

The first naturally occurring arsenic compound to be identified in marine organisms was arsenobetaine, a water-soluble arsenical. It was isolated and identified in the tail muscle of a western rock lobster *Panulirus longipes cygnus* by Edmonds *et al.* in 1977.[8] Subsequently, this compound has been shown to occur in marine animals independently of their feeding habits and trophic level.[1–5,9] In animals of the highest trophic levels, arsenobetaine accounts for almost all the water-soluble arsenic compounds.

On the other hand, the major organo-arsenic compounds in algae have been proved to be arsenosugars.[1–5] Both arsenobetaine and arsenosugars have been proved to be non-toxic.[10,11] This fact indicates the safety of marine organisms or marine products from the point of view of the toxicological aspects of arsenic.

However, there are open questions about arsenic, at least when accumulated in certain algae. An edible brown alga *Hizikia fusiforme*, hijiki (Fucales, Sargassaceae), as well as other brown algae, accumulates large amounts of arsenic.[1–5] However, inorganic arsenic(V) usually accounts for about 50% of the total in hijiki, as well as other members of Sargassaceae.[12] The questions are: (1) why does the family Sargassaceae accumulate high levels of

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toxic inorganic arsenic(V); and (2) why are Japanese consumer not poisoned by eating hijiki?

In the present paper, experiments were undertaken to answer the second question. It is true that this alga accumulates levels of inorganic arsenic(V). However, consumers do not eat the commercial hijiki or the natural form directly: hijiki is traditionally washed and soaked in water for 20 to 30 min before cooking. We investigated the effect of washing and soaking on the arsenic concentration of hijiki.

MATERIALS AND METHODS

H. fusiforme

Commercial hijiki *H. fusiforme* that had been boiled and dried before sale, and natural hijiki were used. Two kinds of commercial hijiki, Me-hijiki (leaves) and Naga-hijiki (branches), were purchased from a market. Natural hijiki were collected from the shore reef of Yoshimi behind the National Fisheries University, Shimonoseki, Japan.

Authentic arsenic compounds

Dimethylarsinic acid was purchased from Nakalai Chemical Co., methanearsonic acid was from Ventron Co., disodium hydrogen arsenate was from Wako Pure Chemicals Co. and arsenic trioxide was from Mallinckrodt Co.

Washing and soaking

An amount of commercial hijiki was soaked in ten times its volume of tap water for 20 min with stirring at intervals. In some experiments, the alga was soaked with stirring in different volumes of distilled water of various temperatures. A certain amount of natural hijiki was also soaked with stirring after rinsing with a small amount of distilled water. The soaked hijiki was filtered through Whatman No. 2 filter paper, and rinsed three times with a small amount of distilled water and analysed for arsenic.

Determination of total arsenic

The arsenic contents were determined after digesting the samples with 2.6 cm^3 of nitric, 0.5 cm^3 of sulfuric and 1.0 cm^3 of perchloric acids. To the residue in the digestion beaker were added 1.0 cm^3 of 25% diammonium hydrogen citrate, 2.0 cm^3 of hydrochloric acid, 0.2 cm^3 of 1 mol dm^{-3} potassium iodide and 0.2 cm^3 of 0.4 mol dm^{-3} stannous chloride; this was diluted with water to a volume of 10 cm^3 to give an arsenic concentration of 10–80 μg dm^{-3}. Arsenic was determined by arsine (AsH_3) evolution–electrothermal atomic absorption spectrometry (Nippon Jarrel Ash, model AA 845).[13] The detection limit for arsenic was 1 ng of arsenic.

Determination of inorganic and methylated arsenic compounds

About 0.1 g of hijiki was digested with 2 cm^3 of 2 mol dm^{-3} sodium hydroxide at 95 °C for 3 h. A portion of the digested arsenicals in the mixture was determined by arsine evolution–cold trap–quartz furnace atomic absorption spectrometry as described by Maeda *et al.*[14] In brief, the arsenicals were reduced with sodium borohydride to the arsine compounds. The arsine gases were frozen out in a batch in a liquid-nitrogen U-trap. The arsines were successively carried out of the trap upon warming it, passed through a quartz tube atomizer and the arsenic content determined using an atomic absorption spectrometer.[9]

RESULTS

Arsenic concentration in the hijiki before and after washing and soaking

Table 1 shows the effect of the normal washing and soaking process (washing/soaking) on the arsenic content of commercial and natural hijiki: 10 g of each sample was washed and soaked with 100 cm^3 of tap water.

The arsenic concentration in the commercial Me-hijiki (leaf) before and after the washing/soaking was 123.4 mg g^{-1} and 49.3 mg g^{-1} of dry tissue respectively. That in the commercial Naga-hijiki (branch) was 147.3 mg g^{-1} and 69.0 mg g^{-1} of dry tissue respectively.

In the natural hijiki, the arsenic concentration in the leaves before and after the washing/soaking was 231.0 mg g^{-1} and 96.5 mg g^{-1} of dry tissue respectively, and that in the branches was 91.2 mg g^{-1} and 59.5 mg g^{-1} of dry tissue respectively.

In the commercial hijiki, which was boiled and dried before sale, and in the natural hijiki, the

Table 1 Arsenic concentration in commercial and natural hijiki before and after washing and soaking

Sample	Concentration (μg g^{-1} of dry tissue)[a]	
	Before	After
Commercial		
Leaf	123.5	49.3
Branch	147.3	69.0
Natural		
Leaf	231.0	96.5
Branch	91.2	59.5

[a] $n = 2$.

washing/soaking process was effective in reducing the arsenic content of leaves and branches: about 32 to 60% of arsenic was removed from the alga.

Effect of water volume

5 g of each kind of commercial hijiki, leaf (Me-hijiki) and branch (Naga-hijiki), were washed with 50, 500, 1000 and 2500 cm^3 of distilled water at 15 °C. As shown in Fig. 1, an increase in the amount of water did not affect the removal of arsenic from the alga in either kind of hijiki.

Effect of water temperature on the commercial hijiki

5 g of each of Me-hijiki and Naga-hijiki were washed with 500 or 2500 cm^3 of water at various temperatures. Arsenic concentration decreased linearly with increase in washing/soaking temperature from 0 to 60 °C and gradually from 60 °C to the temperature of boiling water (Fig. 2). The amount of water to wash and soak (500 or 2500 cm^3) did not affect the removal of arsenic at any washing temperature.

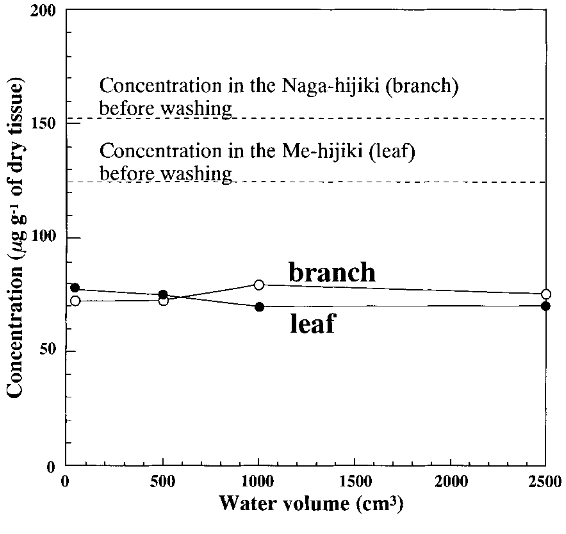

Figure 1 Effect of water volume on the arsenic concentration in 5 g (dry tissue) of washed and soaked commercial hijiki.

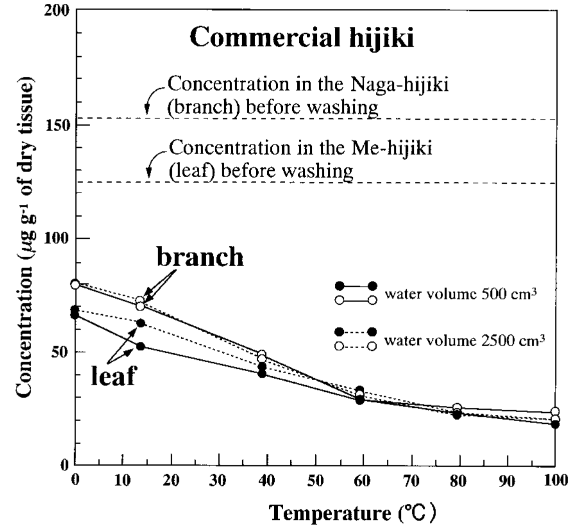

Figure 2 Effect of water temperature on the arsenic concentration in 5 g (dry tissue) of washed and soaked commercial hijiki.

Effect of water temperature on the natural hijiki

As shown in Fig. 3, 5 g of each of the leaves and branches of natural hijiki were washed and soaked with 500 cm^3 of water at various temperatures. The arsenic concentration of the natural hijiki, as well as the commercial hijiki, decreased as the washing temperatures increased from 0 to 60 °C.

Concentration and chemical form

Arsenic compounds in the commercial hijiki were analysed by arsine evolution–cold trap–quartz furnace atomic absorption spectrometry. The concentration and chemical form of arsenic compounds occurring in the hijiki before and after the washing/soaking are shown in Fig. 4. Only arsine and dimethylarsine were detected. In the Me-hijiki (leaf), arsine accounts for 88.5% of the total arsenic and dimethylarsine accounts for 11.5% before the

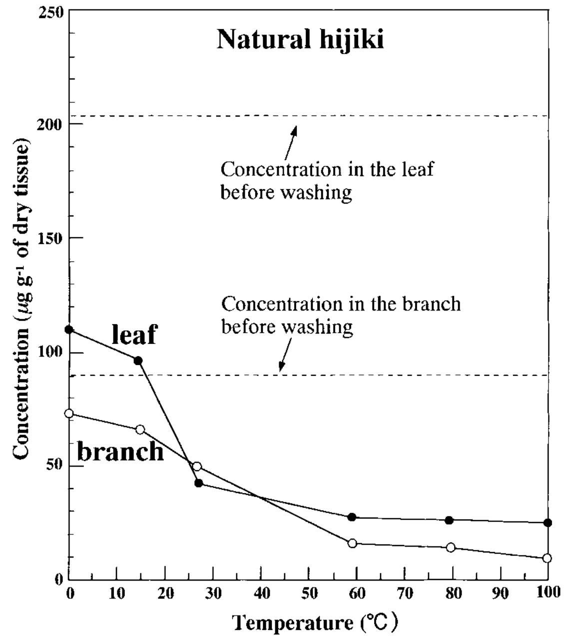

Figure 3 Effect of water temperature on the arsenic concentration in 5 g (dry tissue) of washed and soaked natural hijiki.

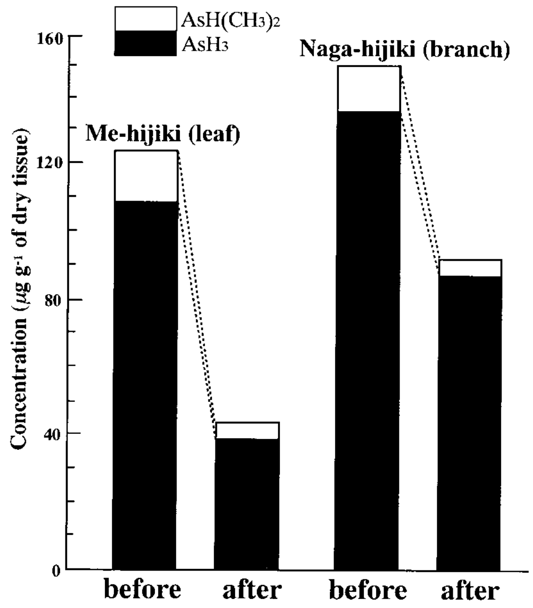

Figure 4 Concentration and chemical form of arsenic in the washed and soaked commercial hijiki.

washing/soaking. They account for 90.8% and 9.2% respectively after the washing/soaking. The extent of the removal of inorganic arsenic was greater in the Me-hijiki than in the Naga-hijiki. On the other hand, there was no significant difference in the extent of removal of the dimethylated arsenic between Me-hijiki and Naga-hijiki.

DISCUSSION

Hijiki has been eaten in Japan from ancient times. This fact may suggest the safety of hijiki itself as food. However, consumers do not eat these algae raw.

In the manufacturing process of commercial hijiki, the algae are collected from the sea shore, boiled (or steamed) and dried. The boiling or steaming process is need to soften the tissues and remove the bitter taste. In Japan, people routinely buy the dried hijiki and make preparations before cooking: it is washed with water and soaked in water or lukewarm water for 20 to 30 min. After draining, the hijiki is stir-fried with seasonings, abura-age (deep-fried tofu) and/or chicken.

The removal of arsenic from hijiki with the washing and soaking was clearly demonstrated in this study, both in the commercial and the natural hijiki: The washing and soaking were essential in lowering the arsenic level of hijiki.

The extent of arsenic removal evidently increased with increase in the temperature of the water used in the washing and soaking. To reduce high contents of arsenic, washing and soaking in hot water at more than 60 °C is recommended. However, soaking in water of too high a temperature may cause the removal not only of arsenic, but also of tasty constituents, resulting in a less palatable dish.

There was no great difference in the final extent of arsenic removal between the commercial and the natural hijiki. This fact means that boiling (or steaming) and drying of hijiki in the manufacturing process may not be essential for lowering the arsenic level, but that the washing and soaking process in each home is essential.

Some people harvest natural hijiki by themselves to eat. In this case they wash and boil them before cooking. This treatment is considered to be very effective at lowering the arsenic level of natural hijiki (Fig. 3): the arsenic level of boiled natural hijiki was lower than that of commercial hijiki washed and soaked in water at room temperatures

(Fig. 2). The reason why the arsenic level is higher in commercial hijiki, which is boiled in the manufacturing process, compared with boiled natural hijiki, may be as follows. When the commercial hijiki is successively harvested and boiled in an iron caldron, the stock in the caldron is not always discarded but repeatedly used to give the product a beautiful black colour. The boiling in concentrated stock is suggested as being unsuitable for lowering the arsenic level of hijiki; commercial hijiki apparently needs to be washed and soaked at home.

Regarding the safety of hijiki as a food, the greatest concern is what the major arsenical is in hijiki after the washing and soaking. About 90% of the total arsenic left in the washed and soaked hijiki was inorganic arsenic and 10% was dimethylated arsenic compound(s). The inorganic arsenic is considered to be the inorganic arsenic(V) originally accumulated in the raw hijiki, whereas the dimethylated arsenic compound(s) is assumed to be arsenosugar(s) or its (their) degradation products, because the major arsenic compounds in hijiki are reported to be dimethylated arsenosugars and inorganic arsenic(V).[15]

We conclude that the decreased arsenic concentration brought about by the washing/soaking of hijiki is, at least, part of the reason why people are not poisoned by ingestion of hijiki; if consumers eat 5 to 10 g (dry weight), of Me-hijiki or Naga-hijiki, a normal amount at a meal, they take only 0.2 to 0.4 mg of inorganic arsenic(V) in the former or 0.33 to 0.65 mg in the latter (lethal dose of arsenic trioxide to adults: 70–180 mg[16]). The chronic effect of arsenic in hijiki is not clear; although the arsenic distribution in rats fed a hijiki diet has been reported,[17,18] information about chronic effects is not available. The hijiki that is sold in Japan is safe as a food provided that consumers continuously adopt at home the traditional preparation methods of washing and soaking, and do not eat it in excess.

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