Studies on the Chemical Forms of Arsenic in Sea Foods and in Urine after Eating These Foods

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Many sea foods, *e.g.* seaweed, shellfish, fish and crustaceans, are eaten in Japan. It has long been known that some of these sea foods contain arsenic at high concentrations, but they are not harmful to humans. There is little doubt that this arsenic is naturally acquired and does not reflect environmental pollution. It has also been recognized that the toxicity of arsenic is dependent on its chemical form and valency state.

In the present study, we analyzed the chemical forms of arsenic in sea foods and in human urine after eating these foods, and also the excretion patterns of arsenic in the urine after eating these foods.

Determination methods for As(III), As(V) and monomethylarsonic acid(MMAA) (BAL chelate method), dimethylarsinic acid(DMAA) (ECD-GC method) and total arsenic (wet digestion with Ni^{2+} and graphite furnace atomic absorption method) have been developed.

Analyses of total As and some arsenic components (As(III), As(V), MMAA and DMAA) in sea foods [Hijiki (*Hizikia fusiforme*), Konbu (*Laminaria japonica*), dried shrimp (*Sergestes lucens*) and flat fish (*Kareius bicoloratus*)] and in urine after eating these foods were carried out by the above methods.

Most of the As(more than 90%) in aqueous extracts of Konbu, shrimp and flat fish existed in unidentified organic bound forms, *i.e.*, not as inorganic and methylated arsenic. A large portion (more than 80%) of that in Hijiki appeared as inorganic arsenate and arsenite (60% and 20%) or substances releasing inorganic arsenicals in acid media (pH 2).

Excretion patterns of As in urine after eating these foods were as follows: in the case of Hijiki and dried shrimp, large amounts of arsenic were excreted as DMAA(42% and 41%), and in the case of Konbu, DMAA accounted for most of the excreted arsenic.

On the other hand, in the case of shrimp and flat fish, over 50% of As was excreted as unidentified organic compounds.

The arsenic in these foods, except for Hijiki, was rapidly excreted in urine(within 40 h after eating), but prolonged excretion was observed in the case of Hijiki. This prolonged excretion is probably due to the presence of a large amount of inorganic arsenicals.

Arsenic excretion ratios from Hijiki, shrimp and flat fish into urine were 51%, 47% and 24.2%. These results suggest that the other arsenic components may be incorporated in the body and/or excreted by other pathways (in feces and expired air).

Furthermore, arsenic components in Konbu, shrimp and flat fish were fractionated. From Konbu, a fraction containing 6.4% As was obtained, and it gave glucose and DMAA upon acid hydrolysis. The main substance in this fraction is presumed to be arseno-oligosaccharide (molecular weight < 1500). An arsenic-containing fraction from dried shrimp appears to be an arseno-oligopeptide, since the fraction gave a positive Ninhydrin reagent and gave arsenobetaine upon acid hydrolysis.

A fraction containing 14.5% As was obtained from flat fish by methanol extraction, active carbon chromatography, gel filtration (Sephadex G-15) and cellulose column chromatography, but structural studies are not yet complete.

The fractions obtained from flat fish and urine passed after eating flat fish by separation as described above showed identical TLC behavior.

In the case of urine passed after eating shrimp, 41% of the total excreted arsenic was DMAA, as described above, and 50% of the unknown excreted arsenic components (26% of total excreted arsenic) was identical with arsenobetaine on TLC.