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Safety Evaluation of Organoarsenical Species in Edible *Porphyra* from the China Sea

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A study was carried out to determine arsenic species in *Porphyra* seaweed originating from the China Sea. Information about arsenic species in *Porphyra* was provided by HPLC-ICP-MS and ES-MS-MS. The total arsenic concentrations of *Porphyra* samples from five different producing areas ranged from 2.1 to 21.6 mg/kg. The analysis report also showed that arsenosugars were the only arsenic species that could be detected in all of the extracts of samples. Arsenosugar PO_4 was the major compound in most samples (0.3−13.9 mg/kg of dry weight), followed by arsenosugar OH (0.7−6.2 mg/kg of dry weight). A further experiment was done to investigate the stability of arsenosugars in the process of being heated. It was observed that the arsenosugars were stable during a short-term heating at 100 °C. Their stability in human ingestion was also studied. A substantial increase of dimethylarsinic acid (DMA) was detected in urine samples collected from six volunteers after the consumption of this seaweed. The results obtained indicated that arsenosugars had been metabolized to DMA, which is more toxic than arsenosugars. From this point of view, consumers should consider the possible adverse effects of edible *Porphyra* on human health and choose those *Porphyra* having lower arsenic concentrations.

KEYWORDS: Arsenic speciation; arsenosugars; edible algae

INTRODUCTION

Algae or seaweeds are very popular in the Chinese and Japanese kitchen. They are mixed in soup or eaten with rice. *Porphyra* is a kind of *Rhodophyta* (red algae), which is the most consumed of all algae. *Porphyra* is named "zicai" (purple vegetable) in Chinese and "nori" in Japanese. It is the focus of a billion-dollar aquacultural industry in the People's Republic of China, Japan, and Korea, making this seaweed the most valuable plant or animal crop grown by cultivation in the sea. In China 16000 tons of dried *Porphyra* are produced annually (*1*, *2*).

Because of the large quantity of *Porphyra* being consumed, its accurate risk assessment is important. A more comprehensive study of the contents and toxicological implications of the arsenic species present in this algae food product currently sold in China may be necessary, which might then be the basis for the introduction of specific sales restrictions.

At the beginning of 20th century, high levels of arsenic (on the order of milligrams per kilogram) were found in marine organisms, which attracted a lot of attention because arsenic is one of the most notoriously toxic elements to humans. However, it occurs in a variety of different forms (*3*). The inorganic arsenic compounds, such as arsenite and arsenate, are toxic and carcinogenic. Ingestion of inorganic arsenic may cause cancer of the skin, bladder, kidney, lungs, and liver (*4*). The U.S. Environmental Protection Agency (EPA) reduced the guideline limit of arsenic in drinking water from the former 50 μg/L to as low as 10 μg/L, which is largely based on inorganic arsenite and arsenate (*5*). If this limit of 10 μg of As/L was applied to seafood, all of it would be unfit for human consumption. The contents exceed the limit by a factor of 1000 times and higher (*6*−*8*). In fact, the major forms in most marine organisms, which are organic arsenic compounds such as arsenobetaine (AsB) and arsenosugars, are considered to be nontoxic (*9*, *10*). For this reason, the determination of the total amount of arsenic in a sample is not sufficient to assess the risk from eating seafood, and speciation analysis is necessary.

Since the 1970s, a variety of arsenicals have been identified from marine animals and algae. For example, tetramethylarsonium ion was found in clams, AsB was found in marine animals, and several dimethylarsinoyl riboside derivatives were found to be the major forms of arsenic in marine algae (*3*). The latter compounds contain a pentose moiety as part of their molecular structure, which explains why they are commonly referred to as arsenosugars (*11*). The four major arsenosugars, 3-[5′-deoxy-5′-(dimethylarsinoyl)-β-ribofuranosyloxy]-2-hydroxypropylene glycol (arsenosugar OH), 3-[5′-deoxy-5′-(dimethylarsinoyl)-

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Table 1. Formulas of Some Arsenic Compounds

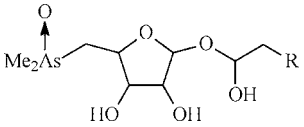
arsenic compd	formula
arsenite (As^{3+})	$As(OH)_3$
arsenate (As^{5+})	$AsO(OH)_3$
monomethylarsonic acid (MMA)	$CH_3AsO(OH)_2$
dimethylarsinic acid (DMA)	$(CH_3)_2AsO(OH)$
arsenobetaine (AsB)	$(CH)_3As^+CH_2COOH$
	
arsenosugar PO_4	R = $OP(O)(OH)OCH_2CH(OH)CH_2OH$
arsenosugar OH	R = OH
arsenosugar SO_3	R = SO_3H
arsenosugar SO_4	R = OSO_3H

Figure 1. Map of the China Sea showing the five sampling locations.

β-ribofuranosyloxy]-2-hydroxypropyl-2,3-hydroxypropyl phosphate (arsenosugar PO_4), 3-[5′-deoxy-5′-(dimethylarsinoyl)-β-ribofuranosyloxy]-2-hydroxypropanesulfonic acid (arsenosugar SO_3), and 3-[5′-deoxy-5′-(dimethylarsinoyl)-β-ribofuranosyloxy]-2-hydroxypropyl hydrogen sulfate (arsenosugar SO_4), found in marine algae are presented in **Table 1**. Among marine algae, differences in their arsenosugar contents have been noted. Arsenosugars OH and PO_4 predominate in *Rhodophyta* (red algae) and in *Chlorophyta* (green algae), and arsenosugars SO_3 and SO_4 are the major compounds in *Phaeophyta* (brown algae) (*12*).

Because in the 16000 tons of dried *Porphyra* purchased and ingested by the Chinese population per year arsenic concentrations in the range of 16−21 mg/kg (*12*) have been detected, it is very important to determine and identify the As species in *Porphyra*. We chose *Porphyra* samples from five main producing areas (Dalian, Qingdao, Zhejiang, Fujian, and Guangzhou), which are distributed in four areas of the China Sea (Bohai Sea, Yellow Sea, East China Sea, and South China Sea). These samples represent almost all of the commercial *Porphyra* products on the Chinese market. **Figure 1** shows more details about the producing areas of the *Porphyra*.

Table 2. Operating Conditions of the ICP-MS, ES-MS-MS, and Chromatographic Systems

Chromatography	
cation exchange column	Ionpac CS10 250 mm × 4 mm i.d. (Dionex, Sunnyvale, CA)
mobile phase	20 mmol L^{-1} pyridinium in water at pH 2.4 with formic acid
anion exchange column	PRP-X100 250 mm× 4 mm i.d. (Hamilton, Reno, NV)
mobile phase	20 mmol L^{-1} NH_4HCO_3 adjusted to pH 10.2 with NH_4OH
flow rate	1 mL min^{-1}
injected volume	50 μL
Inductively Coupled Plasma Mass Spectrometry	
radio frequency power	1200 W
sampler and skimmer cones	nickel
spray chamber	double-pass (Scott type)
argon coolant flow	15 L min^{-1}
argon nebulizer flow	0.96 L min^{-1}
data acquisition mode	graphics (signal intensity vs time)
Electrospray Tandem Mass Spectrometry	
ion polarity	positive
capillary	4200 V, 1 nA
end plate offset	−500 V, 92 nA
scan range	50–600 u
accumulation time	100 000 μ
averages	5 spectra
sample injection rate	10 μL min^{-1}
trap drive	40.2

Cooking and ingestion of seaweed might cause changes in the chemical structure of certain arsenic species into other possibly more toxic species (*13*−*16*). As this may pose a major risk to consumers, the need to carry out research accordingly is obvious.

In the present study the total concentration of As in the samples was determined by means of inductively coupled plasma mass spectrometry (ICP-MS), and the chemical structures of the arsenic species were identified by using HPLC-ICP-MS and ES-MS-MS. The study is valuable for the evaluation of the arsenic risk in seafood for human health.

MATERIALS AND METHODS

Instruments. The HPLC system was an Alltech model 625 metal-free pump (Deerfield, IL) with a six-port valve (Valco) and a 50 μL injection loop (Rheodyne, Cotati, CA). A PRP-X100 analytical and guard anion-exchange column (Hamilton, Reno, NV) and an Ionpac CS10 analytical and guard cation-exchange column (Dionex, Sunnyvale, CA) were used for HPLC-ICP-MS analysis.

The ICP-MS instrument used throughout this study was an Elan 6000 (PE Sciex, Toronto, ON, Canada). Signals at *m*/*z* 75 and 77 were monitored in the graphic mode of the instrument. The signal for *m*/*z* 77 was used to monitor the $ArCl^+$ interference.

The ES-MS-MS instrument used was an Agilent 1100 series LC/MSD trap.

Details of the chromatographic and instrumental parameters are summarized in **Table 2**.

Reagents. All reagents were of analytical grade unless otherwise mentioned. Ammonium bicarbonate and sodium hydroxide were purchased from Beijing ShiJi (Beijing, China). Pyridine was from Shanghai Chemical Reagent (Shanghai, China). Methanol (HPLC grade) was purchased from Tianjin SiYou Biochemical (Beijing, China). Deionized water (18 MΩ, Beijing Shuangfeng pure water equipment factory) was used throughout the experiment. Arsenate stock solutions were prepared from $Na_2HAsO_4 \cdot 7H_2O$ (Sigma, St. Louis, MO). Arsenite ($NaAsO_2$) was purchased from Merck. AsB, monomethylarsonic acid

(MMA) and dimethylarsinic acid (DMA) were provided by the Commission of the European Communities, Standard, Measurement and Testing Programme.

Sample Collection and Preparation. In China, *Porphyra* is rarely sold fresh; most of it has undergone some form of processing varying from simple drying in the sun to being baked in an oven or flame-dried. Then it is usually sold as a rectangular sheet measuring 19 × 21 cm. In this study, the Chinese seaweeds were collected from five different localities: Guangzhou, Fujian, Dalian, Qingdao, and Zhejiang (see **Figure 1**) in July 2001. Three *Porphyra* samples were bought at local public markets of each location and stored at room temperature until analysis.

Determination of Total Arsenic in *Porphyra.* Three subsamples per kind of *Porphyra* were prepared for determination. An amount of 0.5 g of each sample was transferred into 50 mL Teflon centrifuge tubes. Three milliliters of nitric acid and 1 mL of hydrogen peroxide were added. The loosely capped tubes were heated in a microwave oven for 3−4 min at 750 W three times, with a cooling period of 10 min between each heating period. The clear solutions were diluted to 25 mL with deionized water. These solutions were analyzed for total arsenic by ICP-MS. Ir was used as an internal standard. Three replicates per sample were carried out (*11*, *16*).

The accuracy of the measurement was tested by the analysis of a certified reference material, NIST SRM 1571 Orchard Leaves (National Institute of Standards and Technology, Gaithersburg, MD), which has a certified value of 10 ± 2 mg of As/kg. The value we obtained was 9.5 ± 0.3 mg of As/kg.

Extraction of Arsenic Species from Seaweed Samples. The crude seaweeds were rinsed with deionized water to remove the salt and dirt. The wet samples were oven-dried at 50 °C during 18 h and then ground in a stainless steel grinding mill. One gram (dry weight) of each sample was weighed into a 50 mL centrifuge tube, and 20 mL of an H_2O/MeOH mixture (1:1, v/v) was added. The tube was sonicated for 15 min and centrifuged for 15 min. The supernatant was transferred into a 100 mL beaker. This procedure was repeated another two times. The collected supernatant fractions were dried by rotary evaporation. The residue was diluted with a minimal amount of deionized water, weighed, and stored at 4 °C prior to analysis (*11*).

Identification of Arsenic Species by Mass Spectrometry. Extracts of the samples were analyzed by HPLC-ICP-MS. Both anion-exchange and cation-exchange HPLC were applied. Detailed information about the HPLC system is in **Table 2**. The HPLC column was equilibrated with the appropriate eluent for at least 30 min before sample injection (*11*).

The application of electrospray tandem mass spectrometry (ES-MS-MS) to the characterization of the arsenosugars in the HPLC fractions was to confirm its validity by HPLC-ICP-MS. For the MS-MS experiments, selected ion monitoring (SIM) was performed in the positive mode to determine the $[M + H]^+$ ion, and the fragmentary voltage was optimized for the maximum sensitivity. Each sample solution for analysis was prepared by the addition of an appropriate amount of methanol (50%) and formic acid (1%) (*17*−*19*).

Identification of Arsenic Forms in Seaweeds after Heating and in Human Urine. The stored extract of Guangzhou *Porphyra* was heated at 100 °C in an oil bath for 10 min. This procedure imitated the preparation of seaweeds before eating. The sample was then analyzed immediately by HPLC-ICP-MS.

Because urinary excretion is the major pathway for the elimination of arsenic from the body (*15*, *16*, *20*), chemical analysis of urine samples is a convenient approach to the study of metabolism of arsenic compounds. Urine samples were collected from six adult volunteers (five males and one female), who gave their formal consent. All volunteers refrained from eating seafood for at least 72 h prior to commencing the seaweed ingestion experiment. Each volunteer was instructed to collect two or three urine samples during the 12 h before the consumption of seaweed. We used these samples to determine the background concentration of arsenic. Then each volunteer consumed 15 g (dry weight) of *Porphyra* (Guangzhou) heated in one meal (time zero). Following the one-time consumption of *Porphyra*, urine samples (usually midstream) were collected at 3−5 h intervals for the next 4 days or longer. No other seafood was eaten during the experiment. All of the urine samples were stored at 4 °C and analyzed within 48 h. No preservative was added. We determined arsenic species in the urine samples by using a PRP-X100 anion-exchange column on-line with ICP-MS.

Table 3. Total Arsenic Concentration in the Samples (Milligrams per Kilogram as Arsenic Dry Weight) from Different Producing Areas [Mean ± SD (n = 3)]

source	total arsenic (mg/kg)	extractable arsenic (mg/kg)	extraction efficiency (%)
Dalian	4.6 ± 0.6	4.1 ± 0.5	90
Qingdao	5.8 ± 0.8	5.3 ± 0.6	92
Zhejiang	8.9 ± 0.3	8.3 ± 0.4	93
Fujian	2.1 ± 0.1	2.0 ± 0.2	96
Guangzhou	21.6 ± 1.4	20.1 ± 1.2	93

RESULTS AND DISCUSSION

Total Arsenic Contents. The arsenic concentrations in the edible seaweeds and their extracts are listed in **Table 3**. All *Porphyra* species contain high levels of arsenic, ranging from 2.1 to 21.6 mg/kg (dry wt). The sample from Guangzhou contains the highest amount, 21.6 mg/kg, which is almost the sum of the other samples. The four *Porphyra* from other locations have lower levels (<9 mg/kg). The lowest amount of arsenic in these samples is observed in the sample from Dalian, equaling only 10% of the amount of Guangzhou *Porphyra*. The average value of the total arsenic concentrations in these samples is 8.6 mg/kg (dry wt), and the standard variance is 7.7 mg/kg. This is lower than in the literature (*12*) (16−21 mg/kg).

The extraction efficiencies for As in this study are >90%, which shows that the arsenic species present are easy extracted into H_2O/MeOH. This is helpful for the speciation and identification of arsenic (*21*).

Speciation of Arsenic in *Porphyra* Extracts. Because the toxicity of arsenic compounds is very species-dependent, it is important to carry out speciation analysis of arsenicals present in arsenic-containing foodstuffs. Only then can any evaluation regarding the risk to humans be made.

Ion-exchange HPLC was used to separate the different arsenic-containing compounds in the seaweed extracts. An anion-exchange chromatogram of the Guangzhou *Porphyra* extract is shown in **Figure 2A**. It shows two peaks at retention times of around 167 and 240 s. The *Porphyra* extracts were also analyzed with cation-exchange chromatography (**Figure 2B**). Two peaks appear at 105 and 190 s. Because the retention times of these peaks are not the same as those of inorganic arsenic or MMA, DMA, and AsB, we believe that none of these arsenic forms exist in the *Porphyra*. The abundance of every peak in the chromatogram was measured by manual integration (**Table 4**). Only small discrepancies are seen for *Porphyra* between anion and cation chromatographical modes, so it is clear that there are two arsenic compounds present in the *Porphyra* extract. A1 and A2 in the anion-exchange mode are identical to C2 and C1 in cation exchange, respectively.

From the literature (*3*, *12*), we know usually that arsenosugar OH and PO_4 are the main components in *Rhodophyta* (red algae), and the sum of their relative amounts is 97.9−100%. If we had these arsenosugar standards, then we could identify these two arsenic species by matching the HPLC retention times with them. The chromatographic conditions that we used were the same as those in the literature, but the standards are not available. Not only their chemical synthesis but also their isolation and purification originating from biological materials require complex procedures (*22*, *23*). Consequently, appropriate

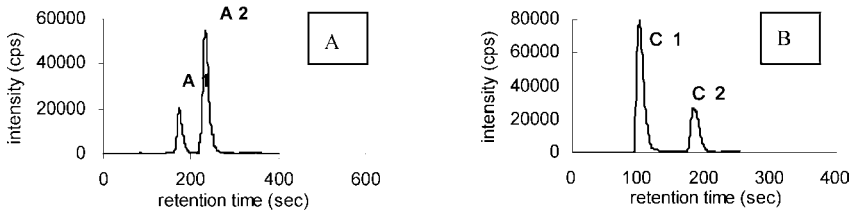


Figure 2. Anion-exchange (A) and cation-exchange (B) HPLC-ICP-MS chromatogram of *Porphyra* (Guangdong).

Table 4. Abundances (Percent) of Each Peak in HPLC Chromatograms and Different Extractable Arsenic Compounds Concentrations (Milligrams per Kilogram as Arsenic Dry Weight) in *Porphyra* [Mean ± SD (n = 3)]

	anion HPLC		cation HPLC		arsenosugar	arsenosugar
source	A1 (%)	A2 (%)	C2 (%)	C1 (%)	PO_4 (mg/kg)	OH (mg/kg)
Dalian	92.9 ± 1.8	7.1 ± 0.6	92.1 ± 1.9	7.9 ± 0.3	0.3 ± 0.1	3.8 ± 0.4
Qingdao	22.2 ± 0.4	77.8 ± 1.6	24.6 ± 0.7	75.4 ± 1.8	4.0 ± 0.4	1.3 ± 0.2
Zhejiang	35.6 ± 1.0	64.4 ± 0.9	37.5 ± 0.6	62.5 ± 1.5	5.2 ± 0.3	3.1 ± 0.2
Fujian	35.7 ± 0.5	64.3 ± 1.2	36.8 ± 0.1	63.2 ± 1.1	1.3 ± 0.1	0.7 ± 0.2
Guangzhou	30.8 ± 0.4	69.2 ± 0.7	31.6 ± 0.3	68.4 ± 1.3	13.9 ± 0.9	6.2 ± 0.4

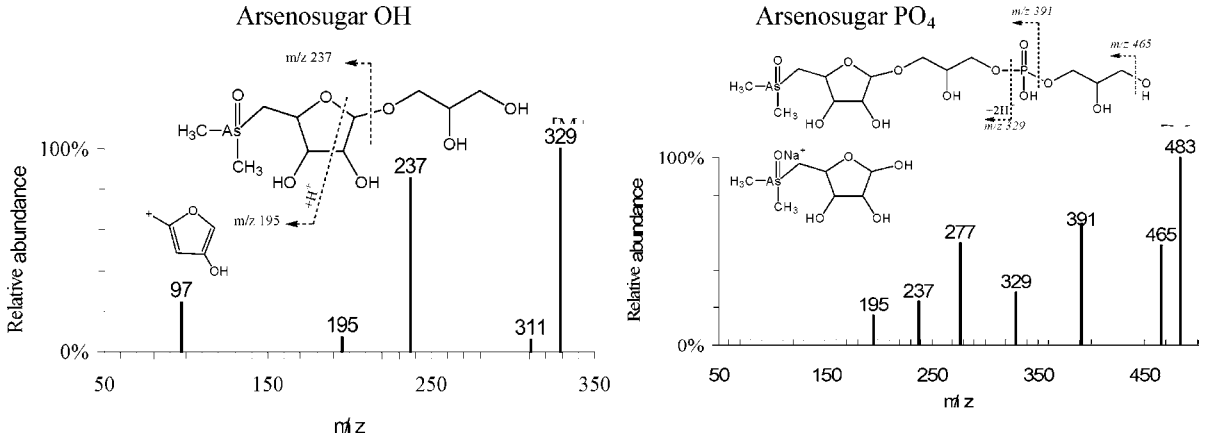


Figure 3. Confirmation of the arsenic compounds by ES-MS-MS: (left) spectrum of A2 (C1); (right) spectrum of A1 (C2).

analytical standards are available in only a few laboratories. Considering the lack of the arsenosugar standards, ES-MS-MS was applied to confirm the identity of the arsenosugars (*17*−*19*).

We collected the eluate of the HPLC column directly at the times corresponding to the retention times of the arsenic species (anion HPLC: A1, 155−180 s; A2, 220−260 s; cation HPLC: C1, 95−120 s; C2, 175−205 s) and then analyzed the fractions by ES-MS-MS. Tandem mass spectra for precursor ions at *m*/*z* 329 and 483 were acquired. Their ES-MS-MS spectra are shown in **Figure 3**. The spectra are similar to those published by Corr et al. and Gallagher et al. (*18*, *19*). Both MS-MS spectra contain *m*/*z* 237 and 195, which are fragments of the dimethylarsinoyl riboside moiety, common to all arsenosugars. The ES-MS-MS spectrum of A2 (C1) shows additional fragments at 465 (loss of water), 391, and 329, which are fragments of arsenosugar PO_4. However, it contains a daughter ion at *m*/*z* 277, which has not been reported in the literature before. One possibility for this difference is that Na^+ from the seaweed was coupled with a fragment of the arsenosugar. Therefore, we can confirm that the two arsenic species in the extract are arsenosugar PO_4 and OH.

The arsenosugars account for the complete arsenic content of the *Porphyra* extract. The presence of the two arsenosugars in the seaweed extracts from different producing areas is more clearly shown in **Table 4**.

The results show that the quantity of arsenosugar PO_4 is higher than that of arsenosugar OH in most *Porphyra* samples. The average ratio of these two arsenosugar concentrations in all *Porphyra* samples is 1.64:1 (arsenosugar PO_4:OH). However, this ratio in Dalian *Porphyra* is 0.079:1 (arsenosugar PO_4:OH). The ratio in the literature (*12*) is 0.22:1−0.72:1.

Identification of Arsenosugar Conversion after Heating Procedures. Our results show that the arsenic species in *Porphyra* are arsenosugar PO_4 and OH, which are essentially nontoxic to humans (*9*, *24*). However, because *Porphyra* is normally mixed in soup or eaten with rice in the Chinese and Japanese kitchen, a heating step is involved. In studies carried out on other arsenic forms subjected to a temperature of 160 °C, Van Elteren and Šlejkovec observed the transformation of AsB into TMAO and $TMAs^+$ and of MMA into As(III) and As(V), species that are more toxic than the original compounds (*25*). To our knowledge no research has been carried out with respect to the stability of arsenosugars after cooking. The extracts of *Porphyra* were heated at 100 °C in an oil bath for 10 min. The temperature and the time are similar to those of the procedure consumers use to treat seaweed before eating. The sample was then analyzed immediately by HPLC-ICP-MS. From **Figure 4** it can be seen that there is no difference between the chromatograms, indicating that the arsenosugars in the *Porphyra* extract remain stable toward short-term heating.

Identification of Arsenosugar Metabolites in Human Urine. It is generally believed that arsenosugars are like AsB in that they are relatively innoxious to humans. However, it should be noted that although humans do not seem to metabolize arsenobetaine, they are able to convert arsenosugars to DMA

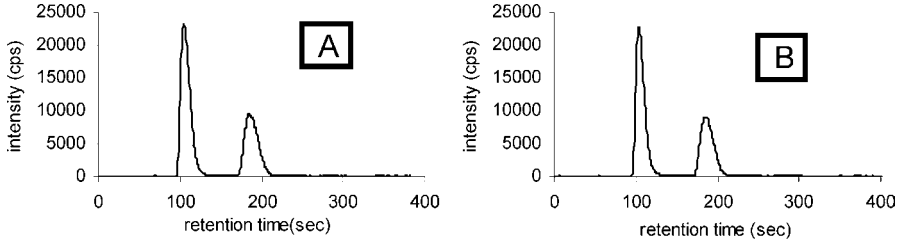


Figure 4. Cation HPLC-ICP-MS chromatogram of *Porphyra* extracts before (A) and after heating (B).

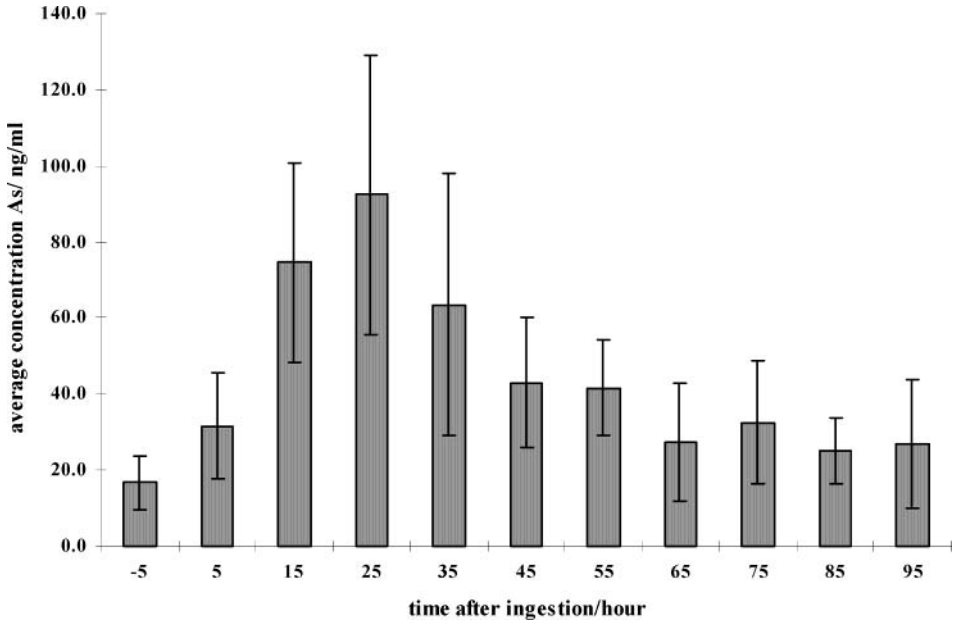


Figure 5. Means and standard deviations of arsenic concentration during each 10 h in urine samples collected from six volunteers after consumption of *Porphyra*.

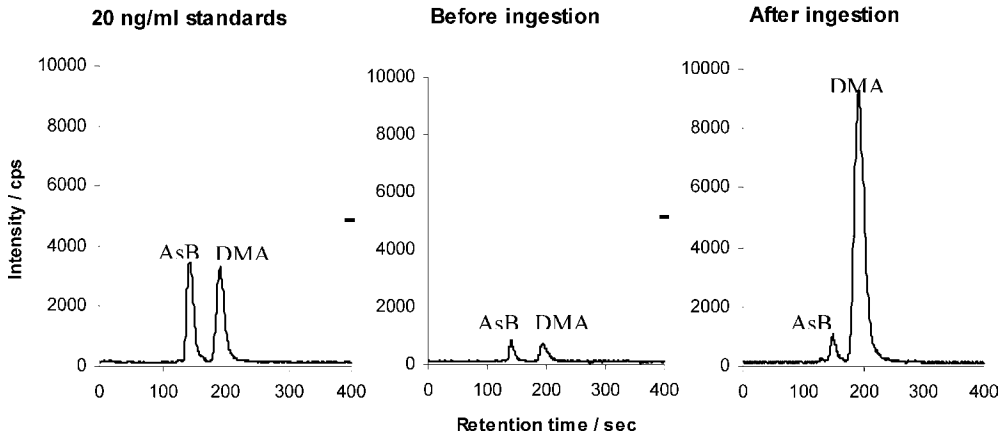


Figure 6. Anion-exchange HPLC-ICP-MS chromatogram of the standard AsB (20 ng/mL), DMA (20 ng/mL), and urine from volunteer 5, collected 3 h before and 26 h after ingestion.

(*15*, *16*, *20*). Recent studies indicate that DMA has the potential to be a human carcinogen and induce DNA strand breaks (*26*, *27*). Therefore, it would also be interesting to evaluate the arsenic risk by studying the metabolites of the arsenosugars in human urine, which is the main excretion route of arsenic from the body.

We obtained urine samples from six adult volunteers (five males and one female). The arsenic metabolites in human urine were monitored over a 4-day period after ingestion of 15 g (dry wt) of *Porphyra* from Guangzhou (containing ~324 μg of arsenic as arsenosugars OH and PO_4) in one meal (time zero). We determined the arsenic in the urine samples by ICP-MS, and results are shown in **Figure 6**. In addition, we counted average values of arsenic concentrations every 10 h from 0 to 100 h after the consumption of seaweed, which is shown in **Figure 5**.

The total arsenic concentration in the participants' urine taken before ingestion was 10−30 ng/mL, which is within the range expected for a person on a nonseafood diet (*15*, *16*, *20*). After ingestion of the seaweed, the arsenic concentrations in urine samples from all volunteers showed immediate small increases. After 10 h, arsenic began to appear in the urine at substantial concentrations, peaking at some point between 18 and 35 h. From our sampling times, 20−30 h gave the highest concentration: 92.5 μg/L (average value of 19 samples collected during

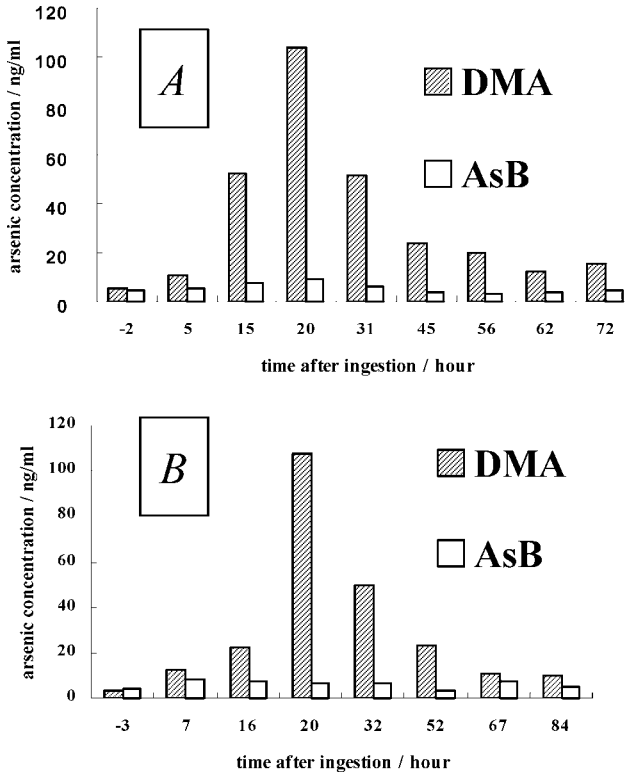


Figure 7. Relative concentrations of the arsenic species in urine samples from volunteers 5 (A) and 6 (B) after consumption of *Porphyra*.

this period). The final urine sample collected after 80 h contained <30 ng/mL, returning to background concentrations.

To further study the excreted arsenic species, we selected urine samples from volunteers 5 and 6 for HPLC-ICP-MS analysis. **Figure 6** shows two typical chromatograms obtained on analysis of the urine sample before and after consumption of *Porphyra*. Other results are shown in **Figure 7**. These samples represent the pattern that was common in most samples. The major peak of **Figure 6** was assigned as DMA by matching the retention time with a standard. The concentration is almost 15−20 times higher than before ingestion. This result indicates that arsenosugars are metabolized to DMA, which is more toxic. Therefore, metabolism and the nature of the metabolites should be taken into consideration in the assessment of the overall toxicological effect of seaweed ingestion. In previous literature DMA has been confirmed to be the major metabolite of some seafoods such as kelp (brown seaweed) and crab, although other unknown metabolites have been detected (*15*, *16*, *20*).

The second major metabolite in the urine had a retention time that matched with AsB standard. However, it is unlikely that the AsB is a metabolite of arsenosugars, because no AsB has ever been found in the urine of people on a seaweed diet (*15*, *16*, *20*). The volunteers were asked to avoid all kinds of seafood before sampling, and they complied, so we think other foods are responsible for the presence of AsB, such as chicken or pork. Because some Chinese feeders use fish bone dust to feed chickens and pigs, the AsB may have been transferred to meals of chicken and pork, which are very difficult to avoid in the Chinese kitchen. Now we are interested in of the presence of AsB in meal, and we are currently studying this.

Conclusion. The concentrations of total arsenic and of the different arsenic species in the extracts of five *Porphyra* food products currently on sale in China were determined. The suitability of the analytical methodologies for this type of matrix was confirmed by evaluating their analytical characteristics. The concentration ranges found for each sample (in dry weight) were 2.1−21.6 mg/kg for total arsenic, 0.3−13.9 mg/kg for extractable arsenosugar PO_4, and 0.7−6.2 mg/kg for extractable arsenosugar OH. The predominant species was arsenosugar PO_4, and the arsenic found in this form represented 62% of total arsenic in this seafood item. In addition, the arsenosugars are stable in short-term heating, so *Porphyra* seems to be a type of safe seafood that does not contain toxic arsenic species.

However, after ingestion of the seaweed, the volunteers' urine arsenic concentrations showed immediate increases. The concentration of DMA is almost 20 times higher than before ingestion. We should consider the possible adverse effects of the metabolites on human health. If consumers choose to eat *Porphyra*, it is recommended that they purchase the *Porphyra* from Dalian or Fujian because of their lower As concentrations.

ACKNOWLEDGMENT

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