Arsenic Circulation in Marine Ecosystems

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Abstract: Microbial conversion behavior was investigated with several standard arsenicals. As typical origin of marine micro-organisms, sediments, macro-algae, mollusk intestine and suspended substances were used. The degradation of arsenobetaine was observed with every origin, suggesting the ubiquitous occurrence of arsenobetaine-decomposing microorganisms in marine environment. Especially, the microorganisms occurring in the sediments and the suspended substances completely degraded it to inorganic arsenic. From these results, it was hypothesized that there is an arsenic cycle that begins with the complete degradation of arsenobetaine to inorganic arsenic.

Key words: arsenic, arsenobetaine, degradation, micro-organisms

1. Introduction

Arsenic occurs ubiquitously in nature, including organisms. Its concentration is much higher in marine organisms than in terrestrial ones, Lunde reported the occurrence of both inorganic and organic arsenic compounds in marine organisms. After that various kinds of organic arsenic compounds were isolated or identified from marine organisms. Nowadays, it is well known that arsenic is accumulated mainly as the organic form in marine organisms. Edmonds et al. accomplished the first important work on the identification of the organic arsenic compounds, the isolation and identification of arsenobetaine from the muscle of western rock lobster. This compound is, at present, considered as the final metabolite of arsenic in marine food chains and is accumulated in marine animals in a greater or lesser degree. We have also confirmed the ubiquitous occurrence of this compound in marine animals independently of their feeding habits and the trophic levels to which they belong. As to the process of biosynthesis of organic arsenic compounds in food chains, it is generally accepted that inorganic arsenic taken from seawater is concentrated and converted to organic arsenic comounds by phytoplankton or algae, further metabolized through the food chains and accumulated as arsenobetaine in marine animals.

In this study, we have tried to approach the fate of arsenobetaine or other organoarsenicals microbiologically. Degradation experiments were performed with synthetic arsenobetaine or other arsenic compounds and each of four kinds of typical origins for marine micro-organisms, namely sediments, marine macro-algae, marine mollusk intestine and suspended substances.

2. Materials and Methods

Origin of microorganisms

Sediments, two species of marine macro-algae (Sargassum fusiforme and Monostroma nitidum), mollusk intestine (Liorophura japonica) and suspended substances were collected from the coastal waters of Yoshimi. Suspended substances was collected from about 2 dm$^3$ of seawater by filtration with a membrane filter (0.22μm). Two bacterial strains were isolated as arsenobetaine-decomposing bacteria from the coastal sediment and were identified as members of the Vibrio-Aeromonas group by means of biochemical reactions and morphological characteristics.

Cultivation

Two culture media were used for the microbial
170 Ken'ichi Hanaoka and Masakatsu Usui

and m/z 82 (16Se) were monitored to detect possible interferences on m/z 75.

1H NMR and 13C NMR spectra were measured on a Bruker AAM‒400 NMR spectrometer in D2O at 400 MHz and 100 MHz respectively with 3-(trimethylsilyl)propionic acid-d4 sodium salt (TSP) as an internal standard. FAB mass spectra were performed with a JEOL JMS DX-300 mass spectrometer equipped with a fast atom bombardment ion source and xenon atoms at 6 keV. A combination of gas chromatographic separation with hydride generation, followed by a cold-trap technique and selected ion monitor mass spectrometric analysis, was also used for characterization of purified metabolites.

Purification and identification of the metabolites

Each medium containing the metabolites as microbial degradation products of arsenicals was centrifuged for 15 min at 3,500 rpm and the supernatant was subjected to various column chromatographies to purify each metabolite.

3. Results and Discussion

Arsenobetaine has been degraded by microorganisms from every origin investigated so far, i.e. sediments, macro-algae, mollusk intestine and suspended substances. In the typical conversion pattern of AB when the microorganisms had a high activity TMAO and DMA were derived by every micro-organisms investigated. Further degradation was observed in sediments and suspended substances where a considerable amount of (or all) AB was degraded to arsenic(V). On the other hand, relatively low degradation activity was shown by the intestinal micro-organisms of chitons Liolophura japonica in ZoBell medium: only TMAO and DMAA appeared, arsenic (V) not being derived. Furthermore, in this case, little conversion was observed in the inorganic-salts medium.

The micro-organisms probably used the carboxymethyl moiety of arsenobetaine to satisfy their requirement for organic carbon, and converted arsenobetaine to TMAO.
After this source of carbon had become exhausted, the methyl groups in TMAO became useful; they could have been cleaved from the arsenic compound, and become utilized by the micro-organisms with concomitant conversion of TMAO to DMAA or arsenic (V). It seems to be a ubiquitous phenomenon that arsenobetaine is degraded to TMAO or DMAA, or even to inorganic arsenic, this being concluded from the following facts:

1. Microorganisms occurring in every origin investigated degraded arsenobetaine to some degree; especially those occurring in the sediment and suspended substances completely degraded it to arsenic (V).
2. The two strains of bacteria isolated from sediment having arsenobetaine-decomposing activity were not unusual members but very common marine bacteria.

If the proposed degradation pathway of arsenobetaine (arsenobetaine→TMAO→DMA→MMA→inorganic arsenic) is assumed in marine ecosystems, and liked to the hypothesis that AB is derived from seawater through food chains, the following hypothesis is necessarily called to mind. An arsenic cycle occurs in marine ecosystems, which begins with the methylation of inorganic on the route to arsenobetaine and terminates with complete degradation of arsenobetaine to inorganic arsenic, both in the sediment and the water column.

The biosynthesis of AB, the final metabolite of arsenic in this cycle, is not always necessary when the fate of organoarsenic compounds is considered. Although arsenosugars\(^5\)\(^-\)\(^7\) or arsenolipids\(^8\)\(^-\)\(^13\) for example, may circulate along this cycle or others, they probably also suffer degradation to inorganic arsenic by the microorganisms without the conversion to arsenobetaine. Thus, all the organoarsenic compounds derived from inorganic arsenic in seawater may have the fate that they, at least in part, finally return to the original form, inorganic arsenic.

5. References


