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Arsenobetaine and thio-arsenic species in marine macroalgae and herbivorous animals: Accumulated through trophic transfer or produced *in situ*?

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ABSTRACT

Arsenobetaine (AB) and thio-arsenoribosides were measured in common macroalgae species (8 phaeophyta, 4 rhodophyta and 2 chlorphyta), along the Australian south east coast line. As well, arsenic species profiles were measured for two common marine herbivores, the sea urchin *Centrostephanus rodgersii* and the fish *Odax cyanomelas* that graze on these macroalgae to understand if trophic transfer of these species would account for their presence in marine herbivores. AB was found in seven of the fourteen macroalgae species investigated but does not contributed significantly to any of the macroalgae arsenic content (0.01-1.2 μg/g). AB was found in only two of the brown macroalgae and all the red and green macroalgae (with the exception of *Corallina officinalis*). Thio-arsenic species were found sporadically, but not in high concentrations in any of the macroalgae investigated. AB present in macroalgae is likely to be associated with epiphytic organisms while thio-arsenoribosides are likely to be produced by decaying parts of damaged macroalgae. A laboratory feeding experiment in which the herbivorous gastropod, *Austrocochlea constricta*, was fed macroalgae containing thio-arsenoribosides for a 24 hr period every three days showed that these are readily accumulated over a short period. Thio-arsenoribosides in herbivores are therefore probably obtained through trophic transfer. Some AB is also obtained through trophic transfer; however, the presence of trimethylated arsonioribosides, a hypothesized precursor of AB formation in herbivores, suggests that some AB is produced within herbivores from the transformation of arsenoribosides accumulated from their diet.

Introduction

Marine macroalgae are a major source of arsenic for herbivorous marine animals in the marine environment. The arsenic species present in marine macroalgae are, therefore, of great importance in the cycling of arsenic within shallow water marine environments.

Marine macroalgae contain mostly arsenoribosides, with minor amounts of inorganic arsenic, dimethyl arsenic and thio-arsenic species (Tukai et al., 2002b). Arsenobetaine (AB), however, has been reported as a minor component of macroalgae (Nischwitz and Pergantis, 2005). Several pathways have been proposed for the formation of AB from arsenoribosides (Fig. 1) although the formation of AB via

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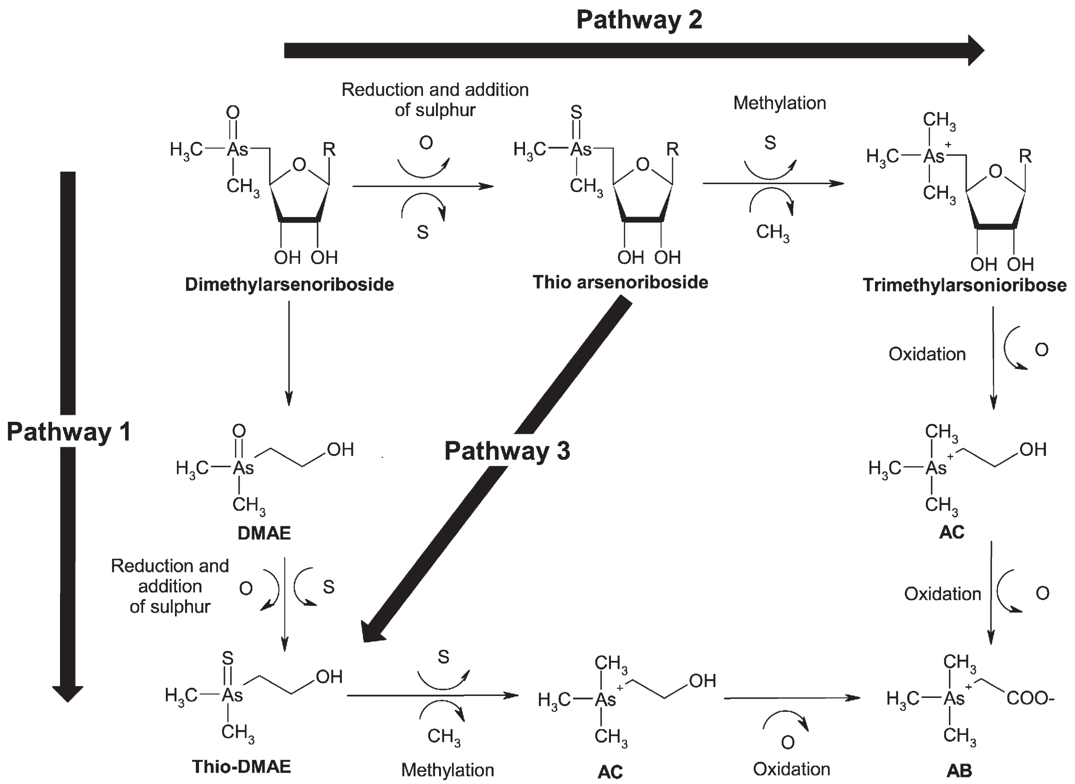

Fig. 1 – Proposed pathways for the metabolism of arsenoribosides and the formation of arsenobetaine in marine animals.

trimethylated arsonioribosides directly from algae is not likely as only one study has reported the presence of trimethylated arsonioribosides in macroalgae (Shibata and Morita, 1988). It would be more likely that these are formed during digestion in organisms. In terms of the trophic transfer and metabolism of arsenic, the reporting of AB must be assessed, as the direct accumulation of arsenobetaine from dietary consumption would explain the occurrence of AB in marine herbivores (Foster et al., 2006, 2008; Kirby et al., 2005). Epiphytes and bacteria are commonly associated with macroalgae (Armstrong et al., 2001; Paerl and Pinckney, 1996) and if not thoroughly removed could be responsible for the presence of some if not all AB in marine herbivores. There is some uncertainty how samples with reported AB concentrations have been cleaned and prepared for chemical analysis. Similarly, thio-arsenoribosides are commonly found in degrading algae (Foster and Maher, 2010) and may have been reported in live algae as it is possible degraded and not healthy live macroalgae specimens were analyzed.

This study reports the occurrence of AB and thio-arsenic species in previously analyzed red, green and brown macroalgae (Tukai et al., 2002a, 2002b) and two herbivores, a sea urchin *Centrostephanus rodgersii* and a fish *Odax cyanomelas* that extensively graze on these macroalgae to understand if trophic transfer of these species would account for their presence in marine herbivores. A feeding experiment was also conducted in which the herbivorous gastropod, *Austrocochlea constricta*, was fed decaying macroalgae containing thio-arsenoribosides to determine if they readily accumulate these arsenic species.

1. Materials and methods

1.1. Sampling

Macroalgae, fish (*O. cyanomelas*), black sea urchin (*C. rodgersii*) and gastropods (*A. constricta*) were collected from Mosquito Bay, Wimbie, and Lilli Pilli on the south coast of New South Wales Australia. Macroalgae were collected by hand from the intertidal zone (Tukai et al., 2002b) and care was taken to select only living undamaged specimens. Sea urchins were collected by hand from the adjacent subtidal zones and fish from the subtidal zone using a spear gun. All samples were placed in clean plastic bags and transported to the laboratory on ice in a cooler.

1.2. Thio-arsenic feeding experiment

Approximately 20 g of fresh *Hormosira banksii* was placed into 500 mL plastic storage containers with 100 mL of unfiltered seawater. The algae were allowed to decay at room temperature (22–25°C) over an initial period of 11 days before being fed to the gastropods. *A. constricta* were kept in an aerated aquarium and placed on the decaying algae at day 12, day 15 and day 21. The gastropods were allowed to feed for 24 hr before being removed, deshelled and frozen. The algae and seawater were collected from each of the containers at the time of collection of the gastropods (data has been previously reported for the water and algal degradation products (Foster and Maher, 2010)).