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Review

Natural occurrence of arseno compounds in plants, lichens, fungi, algal species, and microorganisms

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Abstract

Naturally occurring both water- and lipid-soluble arseno compounds, as well as simple methylated arsenicals, which are less toxic than the inorganic species, and arsenoribosides are considered to be non-toxic, consisting of an interesting group of organometallic compounds. These compounds are of great interest, and the structure, function, and also metabolism, partly, has been elucidated. This review focuses primarily on the presence and distribution of organoarsenic compounds in vascular plants, marine and freshwater algal species, lichens, fungi, and microorganisms. Some aspects of the metabolism and transformation of arsenic species in mentioned organisms will also be discussed.

Keywords: Plant; Lichens; Fungi; Algae; Microorganisms; Arseno-compounds

1. Introduction

Arsenic (**As**) is widely distributed in the lithosphere, hydrosphere and biosphere [1]. Arsenic, the 33rd element, is synonymous with poison. Discovered in 1250 by Albertus Magnus, it has a colorful history, as it is reputed (but unlikely) to be the cause of death of such notables as Napoleon and the American president Zachary Taylor. In the early literature, there are numerous reports of arsenic compounds being used to help reduce fever, Black Death, boils and even improve general appearance and 'well-being'. However, there is no doubt that it is most known for its toxicity, which was recognized even by the ancient Greeks, who preferred to have 'dispensable' slaves work in their mines. The use of arsenic to poison political opponents and other adversaries must have also been common, as specific laws were passed in the 14th and 15th centuries to stop such activities. Such criminal uses of arsenic have led to its being equated with poisoning in the public's mind. When more then 1000 people were poisoned by beer in 1900, it was assumed that arsenic was the cause [2].

Arsenic can enter terrestrial and aquatic environments through both natural formation and anthropogenic activity. Arsenic species are bioactive and toxic. The chemical and biochemical properties of the arsenic species found in the biological samples are important. In particular, the toxicity of arsenicals will depend on its form, ranging from highest to lowest toxicity, arsines, inorganic arsenites, organic trivalent compounds (arsenoxides), inorganic arsenates, organic pentavalent compounds, arsonium compounds and elemental arsenic. The more soluble forms are typically more toxic. Arsenicals are mostly unstable and degrade or weather rapidly to form arsenate. The inorganic forms of arsenic are more mobile than the organic forms and hence pose more of a risk of leaching into groundwater. An extensive discussion of the chemical and toxicological characteristics of arsenic can be found in a recent review [3]. Arsenic behaviour and its transformations in soil and dependence on different physico-chemical soil properties have been widely investigated [4].

Plants that accumulate metals to high concentrations are sometimes referred to as hyperaccumulators. The term was first used by Brooks et al. [5] to describe those plants that take up and accumulate more than 1000 μM As g^{-1} dry weight (DW). There have been several reports of arsenic hyperaccumulating plants growing on mine wastes

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from various sites in the United Kingdom [6]; in smelter wastes in northeast Portugal [7]; near a copper mine site in northern Peru [8]; and on a site contaminated with chromated copper arsenate wastes in Florida [9]. Although the first three studies of arsenic hyperaccumulators dealt with grasses, the study by Ma et al. [9] there were the first to report an arsenic-hyperaccumulating fern species and, additionally, they discussed the phytoremediation potential of such plants. Different plant parts showed different abilities to accumulate arsenic species. Recent studies have shown that inorganic arsenic compounds are the most important ones in the soil–plant system [4,10]. Marine products usually have high arsenic contents because marine organisms generally accumulate much more arsenic in their tissues and organs than do terrestrial organisms [11–14].

Recent investigation has shown that the arsenic compounds in terrestrial and aquatic plants, lichens, fungi, and algal species are classified into water-soluble and lipid-soluble compounds, and arseno-containing compounds [3,11,12] also are an interesting natural products.

This paper attempts to review the published literature on the variability of arsenic structures of unusual and rare organoarsenic compounds found in particular plants, lichens, fungi, algal species, and microorganisms.

2. Determination of the arsenic species

It is accepted nowadays that the total concentration of an element does not decide its toxic behaviour, rather, the determination of the individual species is necessary, since their toxicities may be very different. Of the studies reported, those for arsenic species probably are of the greatest importance, because the inorganic species, As(III) (No. **1** in Fig. 3) and As(V) (No. **2** in Fig. 3), are notably more toxic than the organic ones, monomethylarsonate (**7**) and dimethylarsinate (**8**), which show a moderately low toxicity, or arsenobetaine (**12**) and arsenocholine (**13**), which are not toxic.

The complex metabolism pathways and bioaccumulation of arsenic have resulted in the occurrence of more than 25 different species of this element in a broad concentration range (up to hundreds of micrograms per gram weight) in plants, freshwater, and marine algae [1,11,12].

2.1. Extraction of arsenic species

2.1.1. Extraction of the water-soluble compounds from plants

A typical extraction procedure of arsenic species from plants usually use the dried and/or powdered leaves or roots extracted by a mixture of a methanol–water (80:20, v/v) for 10–24 h on a cross-shaped rotor or shaker. The mixture was centrifuged for 10–15 min at 3000–5000 rpm, and the supernatant transferred to a round-bottomed flask and evaporated under low pressure to dryness. The residue is treated with Milli-Q water, filtered, and use for HPLC analysis [10].

2.1.2. Extraction from cyanobacteria and/or algal samples

The commercial cyanobacterial powder of *Nostoc* sp. (0.5–1 g DW) was extracted by a methanol–water mixture (1:1, v/v), and was centrifuged for 10 min. After centrifugation, the extract was removed and placed in a round-bottom flask. The extraction procedure was repeated an additional four times for each sample. The combined extract was evaporated to dryness and dissolved in 10 ml of deionized water prior to further analysis [15].

2.1.2.1. Acid digestion. Dry Nostoc (0.25 g) or the residue after H_2O/MeOH extraction (0.5 g) was placed in round-bottom flask fitted with the special condenser, Teflon capillary, four Teflon plugs and a Teflon adaptor [15]. For sampling, an acid mixture of $H_2SO_4/HNO_3/H_2O_2$ (10:30:30, v/v/v) was added and the reaction mixture was refluxed for 2 h, cooled and made up to 25 ml for further analysis.

2.1.3. Extraction of the lipid-soluble compounds from algal species

The algal powder (100–200 mg) was extracted with 3–6 ml water, and a mixture was centrifuged ($50,000 \times g$, 30 min) and the supernatant transformed to a tube. The extraction procedure was repeated on the pellet from this first centrifugation. The resulting pellet was freeze-dried and analyzed for total arsenic. Some of the pellets from the aqueous extractions were further extracted with a mixture of chloroform–methanl–water in an ultrasonic bath (30 min), and the mixture was then centrifuged to separate the two layers. The chloroform layer was transferred to a tube and washed with water. Centrifugation ($4500 \times g$, 15 min) produced a clear chloroform layer, and was used for analysis of arsenolipid compounds [16].

2.2. Methods of separation and identification of arsenic species

Most instrumental methods for arsenic speciation are based on the separation techniques such as high performance liquid chromatography, and gas chromatography–mass spectrometry coupled with sensitive and selective detection systems like hydride-generation atomic absorption spectrometry and inductively coupled plasma.

High performance liquid chromatography combined with inductively coupled plasma (ICP) MS detection (HPLC–ICP–MS) has been the primary analytical technique used to study speciation, that is the determination of one or more individual chemical species, of arsenic in biological materials [14,17a,b,18,19a,b]. The limitations of this technique have, however, been rapidly appearing with the increasing number of studies of natural samples. They include a risk of co-elution of arsenic species, the impossibility of identifying species for which standards are unavailable, and a risk of misidentification of species based on the retention time matching with standards. Successful separation and identification of arsenosugars in two brown

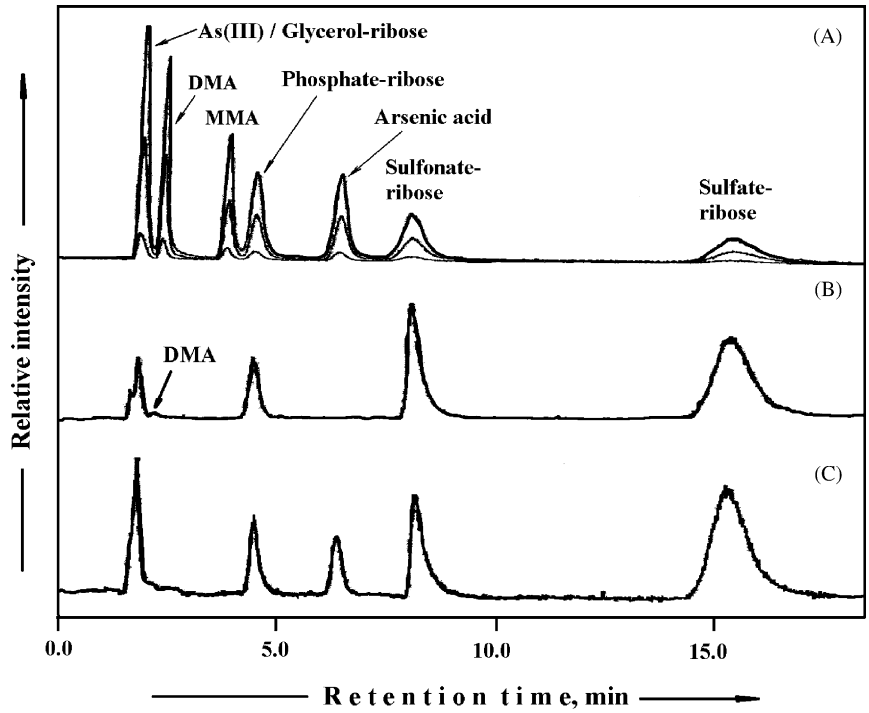

Fig. 1. Separation of arsenosugars in algae using an anion-exchange chromatography [19]. HPLC chromatograms of standard solutions of the arsenic compounds of 1.0, 5.0, and 10.0 ng As/ml of each compound (A), and water/methanol extracts from brown algae *Fucus spiralis* (B) and *Halidrys siliquosa* (C) contains arsenosugars. Adapted by authors.

algae has recently been demonstrated using anion-exchange chromatography [19a] (Fig. 1). Retention time of standard arsenic compounds can be used for identification of unknown natural arsenic compounds from algae.

In terms of identification of arsenic species, the pioneering works used NMR and X-ray crystallography, which required processing kilograms of samples [20,21]. Alternatives, on the analytical laboratory scale, began appearing in

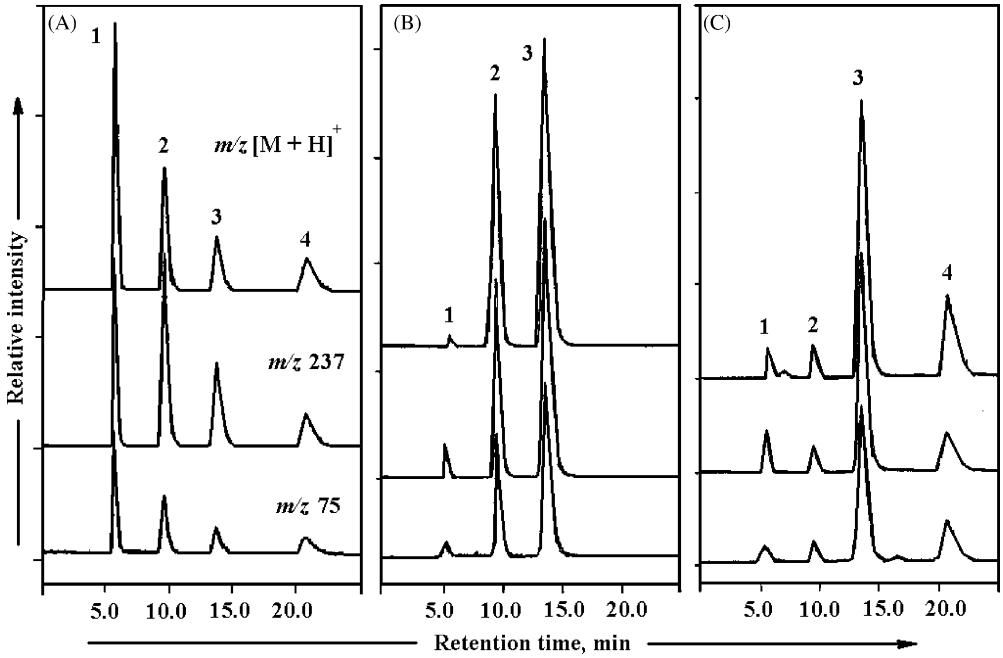

Fig. 2. Liquid chromatography–electrospray ionisation-mass spectrometry chromatograms of arsenosugar standards (A), and crude extracts from two species of brown algae, *Laminaria digitata* (B) and *Fucus vesiculosis* (C) measured at *m/z* 75, *m/z* 237, and *m/z* $[M + H]^+$. Numbering on figure: 1, glycerol-ribose; 2, phosphate-ribose; 3, sulfate-ribose, and 4, sulfonate-ribose (adapted by authors).

the late 1980s with the wider availability of mass spectrometry, employing desorption [22], fast atom bombardment (FAB) [23] and electrospray (ES) ionization [24–26]. However, although mass spectra were abundantly published, successful attempts of identification of arsenic species in biological matrices were scarce. The studies lacked a comprehensive approach and were limited to individual target compounds. The use of FAB–MS enabled Pergantis et al. [23] to identify one arsinoyl-riboside in a *Sargassam* extract the positive ES–MS identification of another riboside could not be confirmed by HPLC–ICP–MS. The work of McSheely et al. [27] described two arsenosugars in *Hizikia* and *Laminaria* algae, which were detected by ES MS/MS after two-dimensional HPLC [28,29]. The same sugars were detected independently in *Laminaria* and one more in *Hizikia* algae by LC–ES–MS using variable fragmentor voltages to allow controlled fragmentation of analyzed species [30]. Separation and identification of four major natural arsenosugar species are shown in Fig. 2. Arsenosugars also can be detected using HPLC–HG–AFS (atomic fluorescence spectrometry) [31], and gives good results.

A recent review discusses the accepted techniques for the speciation of arsenic in biological tissues and the need for quality assurance of speciation analyzes. Quality control is also discussed, focusing on the use of certified reference materials. Also included is validation of methods, and reference material certification involves the participation of several laboratories, enabling the evaluation of state-of-the-art analytical techniques [17b].

3. Occurrence of arseno compounds in plants, lichens and fungi

Arsenate (No. **2** in Fig. 3) is taken up via the phosphate transport system and is incorporated into energy transfer

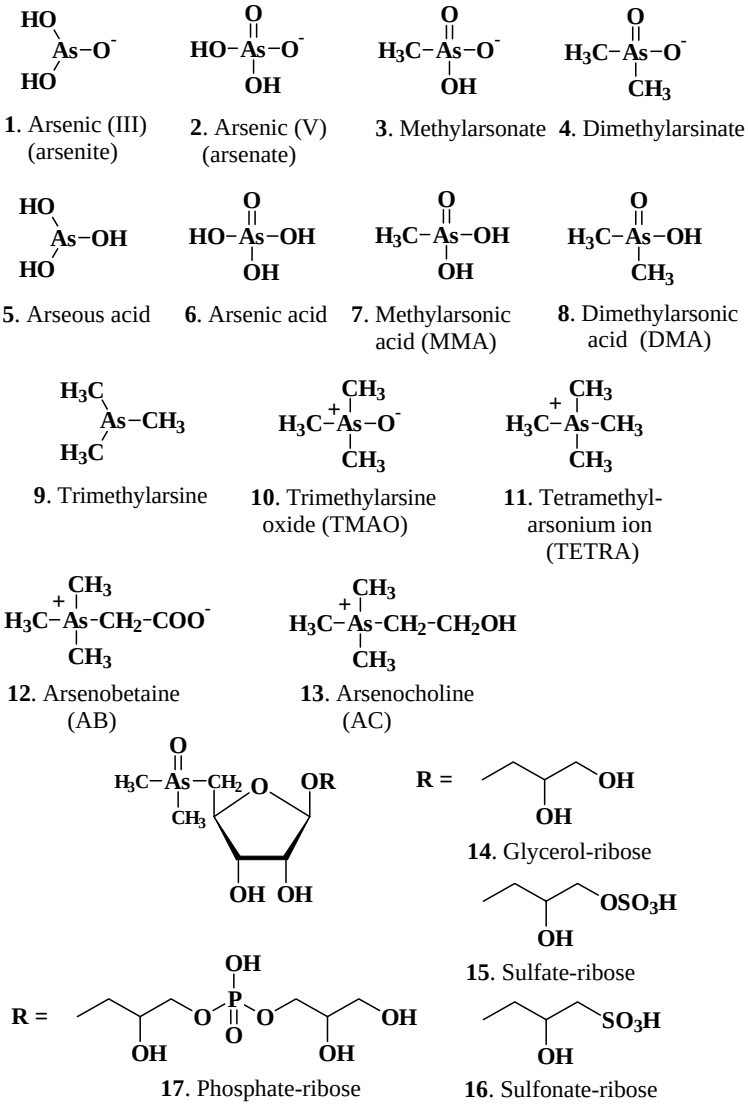

Fig. 3. Inorganic and organoarsenic species isolated from plants, lichens and fungi.

phosphorylation reactions. Arsenite (**1**) inactivates many enzymes because of its having a high affinity for thiol groups of proteins. In terrestrial plants, arsenate is preferentially taken up four times the rate of arsenite **1**. In the presence of phosphate, arsenate uptake is inhibited, in the presence of arsenate, while phosphate uptake is only slightly inhibited. There is a competitive interaction between arsenic and phosphate for the same uptake system in terrestrial plants. The mode of toxicity of arsenate is to partially block protein synthesis and interfere with protein phosphorylation, but the presence of phosphate prevents this mode of action [1,13].

Terrestrial plants growing on shores bordering arsenic-contaminated water show relatively little arsenic content despite the fact that sediments may contain levels as high as 200 $\mu g\ As\ g^{-1}$ [31]. Furthermore, the resistance to arsenic can be increased by acclimating plants to successively higher concentrations of different arsenic species. Little bluestem, *Andropogon scoparius*, can survive in soil containing up to 41,200 $mg\ kg^{-1}$ of arsenate [32]. The soil matrix plays an important role in the availability of arsenic to plants. Retort oil has high concentrations of arsenic but plants grown on these soils show little accumulation, ranging from 0.03 to 0.44 $mg\ kg^{-1}$ [33].

Geiszinger et al. [34] have been studying plants and soil collected near ore vein in Gasen (Austria), and concentration of total, inorganic, and organoarsenic species. The arsenic concentration in the soil ranged from 700 to 4000 $mg\ kg^{-1}$ on DW, and arsenic concentrations in plant species ranged from 0.5 to 6 $mg\ kg^{-1}$ on DW and varied with plant species and the plant part investigated. The extracts of the plants: *Trifolium pratense*, *Dactylis glomerata*, and *Plantago lanceolata* contains inorganic arsenic as arsenic (III), arsenic (V), besides the simple methylated compounds (see Fig. 2): methylarsonic acid (**7**), dimethylarsenic acid (**8**), trimethylarsine oxide (**10**), the tetramethyl-arsonium ion (**11**), arsenobetaine (**12**), and arsenocholine (**13**). More than 62% arseno-containing compounds were found as organoarsenicals in *Trifolium pratense*. The main organoarsenical detected in *Dactylis glomerata* and *Plantago lanceolata* was DMA (**8**). Small amount of AB (**12**), TMAO (**10**) and TETRA (**11**) were present in all three species, whereas AC (**13**) was only detected in *Plantago lanceolata*.

Twelve green plants, namely *Achillea millefolium*, *Alnus incana*, *Asplenium viride*, *Dryopteris dilata*, *Deschampsia cespitosa*, *Equisetum pratense*, *Fragaria versa*, *Larix decidua*, *Picea abies*, *Rubus idaeus*, *Vaccinium myrtilis*, and *Vaccinium vitis idaea* as well as two lichen species, *Alectoria ochroleuca* and *Usnea articulta* have been examined for the presence organoarsenic compounds [35]. All green plants and lichens contain arsenous (**5**) and arsenic acids (**6**), MMA, DMA, AB, TMAO, and glycerol-ribose (**14**) (max in lichen *A.ochroleuca*, 77 $\mu g\ kg^{-1}$ DW). Arsenocholine (**13**) and three arsenoribose species (**14**–**16**) were not detected in the samples.

The water-soluble fractions of plants were analyzed for arsenic species from Yellowknife, Northwest Territories in Canada [36]. Terrestrial plants: *Agrostis scabra*, *Hordeum jubatum*, *Rubus idaeus*, and *Potentilla fruticosa* contain mainly inorganic arsenic (III) and arsenic (V) in range from 24 to 76% (of total arsenic). MA was found in *A. scabra* (0.6%) and *Hordeum jubatum* (3.6%). Terrestrial grasses: *Bidens cernua*, *Carex* sp., *Equisedum fluviatile* and *Typha latifolia*, as well as terrestrial plants, contain inorganic arsenic species (**1**–**3**), and MMA. Among aquatic plants (submergents) such as *Lemna minor*, *Myriophyllum* sp. and *Sparganium augustifolium* arsenosugars were found: glycerol-ribose (**14**) and phosphate-ribose (**17**), and as well as inorganic arsenic and MMA. One species of Bryophytes, *Drepanocladus* sp. contain the highest level of arsenic, 490–1220 ppm DW, concentrations that are remarkably higher than those for other plants. The higher concentrations of *Drepanocladus* sp. compared with that of another plant (horsetail, *Equisedum fluviatile*) collected from the same location might suggest that mosses accumulate more arsenic than other plants [36].

Levels of total arsenic and arsenic species were determined in terrestrial fungi, *Paxillus* sp., *Psathyrella* sp., *Leccinum* sp., *Coprinus* sp., *Lycoperdon* sp. (Giant Mine), and *Lycoperdon* sp. (Con Mine) from Yellowknife, Northwest Territories in Canada [37]. The mushroom *Lycoperdon* sp. from the Giant Mine tailings pond also contained a proportionally higher amount of arsenate, although the major arsenic species in both specimens of *Lycoperdon* sp. was AB. Arsenobetaine was also observed to be the major arsenic species extracted from *Lycoperdon echinatum* (78%), *Lycoperdon perlatum* (88%) and *Lycoperdon pyriforme* (62%); minor components included As (III), As (V), MMA and DMA [38]. A greater variety of arsenic species was observed in the *Lycoperdon* sp. from Giant Mine tailings pond than in *Lycoperdon* sp. from the Con Mine tailings pond. The specimen from the Giant Mine tailings pond was observed to be in a more mature form, and this may account for the differences in speciation observed. Again, the microbial environment influencing the fungus may also have caused differences in arsenic speciation. The arsenic speciation was determined for water-soluble species in the shaggy mane mushroom *Coprinus comatus* for the first time–the major arsenic compound was arsenobetaine (88% of extracted arsenic). Minor components included inorganic arsenic (**1**,**2**,**5**,**6**), DMA, arsenocholine and an unknown arsenic compound. *Paxillus involutus* grew in a next to the Con Mine effluent stream. Its arsenic content was unusual because a major proportion of arsenic extracted (36%) was in an unidentified form (unknown compound Y). An unknown peak possessing a retention time similar to that for unknown Y, on an almost identical chromatographic system, was observed in mussels by Larsen et al. [39]. The authors established that the compound was neither 2-dimethylarsinylethanol [$Me_2As(O)CH_2CH_2OH$] nor glycerylphosphorylarsenocholine [$Me_3As^+CH_2CH_2O\text{-}PO_2{}^-OCH_2CHOHCH_2OH$].

Samples of the edible mushroom *Laccaria amethystina*, which is known to accumulate arsenic, were collected from two uncontaminated beech forests and are an arsenic-contaminated one in Denmark [40]. Three mushroom species from two old arsenic smelter sites in Austria were analyzed for arsenic compounds [41]. *Collybia maculata* contained 30.0 mg, *Collybia butyracea* 10.9 mg and *Amanita muscaria* 21.9 mg As kg DW. In *Collybia maculata* almost all the arsenic is present as AB. *Collybia butyracea* contained mainly AB (8.8 mg As kg^{-1} DW) and dimethylarsinic acid (1.9 mg As kg^{-1}). Arsenic compounds have also been identified and quantified in the mushroom *Amanita muscaria*, collected close to a facility that had roasted arsenic ores [42]. Total arsenic was determined by radiochemical neutron activation analysis in 50 mushroom species (56 samples) from Slovenia, Switzerland, Brazil, Sweden, Netherlands and USA [38]. Arsenic concentrations ranged from 0.1 to 30 mg g^{-1} DW. Arsenic compounds were determined in methanol extracts from the mushrooms by HPLC–ICP–MS. The main arsenic compound found in many mushrooms (various puffballs, genera Agaricales and Aphyllophorales) was AB. Arsenate was the main arsenic species in *Laccaria fraterna* and *Entoloma rhodopolium* and arsenite in *Tricholoma sulphureum*. A mixture of arsenite and arsenate was present in *Amanita caesarea*. Dimethylarsinic acid and methylarsonic acid were present in many mushrooms, but generally as minor components. In *Laccaria laccata*, *Leucocoprinus badhamii* and *Volvariella volvacea*, DMA was the major metabolite. Arsenocholine and the tetramethylarsonium ion were present in a few species, generally at low concentrations, except for *Sparassis crispa*, in which AC was the main compound. Trimethylarsine oxide was not found in any of the mushrooms. In some species small amounts of unknown compounds were also found (see Table 1).

Some lichen species from different locations Yellowknife have also been studied for the presence of arsenic species [37]: *Cladonia* sp. (West Con Mine outflow), *Cladonia* sp. (South Con Mine outflow), *Cladonia* sp. (Con Mine tailings pond), *Cladina* sp. (Beside Con Mine tailings pond), Lichen 4 (name not determined, Giant Mine tailings pond). The major arsenic species in lichens were arsenite and arsenate, with the sum of these two species making up from 62 to 93% of the total extracted arsenic for the lichen specimens analyzed. Arsenobetaine was found for the first time in lichens; it was present in all the lichens samples. Arsenosugar glycerol-ribose (**14**) was present in minor amounts in two lichens from the Con Mine area. Arsenosugars were not detected in lichens growing on beside Con Mine tailings pond. The proportion of As(III) was similar for all samples (42–61% of extracted arsenic), but a broader range was observed for the relative amounts of As(V) in the lichens (12–44% of extracted arsenic). The similarities in arsenic speciation between these three lichens might be expected, due to their common environment. The Giant Mine lichen extract contained mainly As(V) and a small proportion of AB (0.5%). Differences in arsenic speciation between lichens may have been caused by differences in lichen species, and/or differences in their environments. For example, the major form of arsenic was probably as arsenate adsorbed onto ferric hydroxide in the Giant Mine tailings, [43] which may have led to the predominance of arsenate in the tailings water. Unlike Lichen 4, the Con Mine lichens were less likely to herein be submerged in tailings pond water.

Levels of arsenic in the waters of Meager Creek hot springs, British Columbia, Canada, were found to be naturally elevated [44]. Biota including microbial mats, green algae, sedge *Scirpus* sp., cedar *Thuja plicata*, fleabane *Erigeron* sp, monkey flower *Mimulus* sp., moss *Fumaria hygometrica*, mushrooms: *Fomitopsis pinicola*, *Pluteus cervinus*, *Tarzetta cupularis*, and lichen species: *Alectoria* sp., *Bryoria* sp.. *Cladonia* sp. was expected to be impacted by the water, were analyzed for total levels of arsenic and for arsenic species. The major arsenic species extracted from all samples were arsenate and arsenite, which are toxic forms of arsenic. Additionally, small amounts of arsenosugars glycerol-ribose and phosphate-ribose (up to 10 and 2.4 μg g^{-1}, respectively), were detected in microbial mats and green algae. Low to trace amounts of arsenosugars glycerol-ribose and phosphate-ribose were detected in lichens *Alectoria* sp., *Bryoria* sp. *Cladonia* sp. and the fungus *Tarzetta cupularis*.

Microbial mats have been described as ‘heterotrophic and autotrophic communities, dominated by cyanobacteria which an annealed tightly together by slimy secretions from various microbial components’ [45]. The microbial compositions of mats from Yellowstone National Park and elsewhere have been found to depend on pH, temperature, and H_2S concentration in the water [46]. Based on those factors, microbial mats at Meager Creek possibly contain cyanobacteria species such as *Synechococcus lividus*, the photosynthetic green non-sulfur bacteria *Chlorflexus* sp. and the purple bacterium *Chromatium tepidum* [46]. However, the mats are almost certainly not homogeneous with respect to time or area and many other bacteria are present, as mentioned earlier. The high proportion of inorganic species, especially arsenate, is also common in marine algae. Authors concluded that arsenosugars are apparently formed by cyanobacteria and/or bacteria, possibly by algae in lichens *Cladonia* sp., *Bryoria* sp. and *Alectoria* sp., and possibly by the fungus *Tarzetta cupularis*. The arsenic speciation in vascular plants is mostly inorganic arsenic in an amount of at least 13–67% of the total arsenic and significant amounts of arsenite are present in almost all plant samples [44].

The fern *Pityrogramma calomelanos* is a hyperaccumulator of arsenic that grows on arsenic-contaminated soils in the Ron Phibun district of southern Thailand. *P. calomelanos* accumulates arsenic mostly in the fronds (up to 8350 μg As g^{-1} DW) while the rhizoids contain the lowest concentrations of arsenic (88–310 μg As g^{-1} DW) [47]. The arsenic accumulated in the fern rhizoids was approximately

Table 1
Distribution of arsenic species among wild mushrooms ($\mu g\,g^{-1}$ DW) [37,38]

Mushroom	Total As	(**1**) As(III)	(**2**) As(V)	(**7**) MA	(**8**) DMA	(**11**) TETRA	(**12**) AB	(**13**) AC	Unknown
Basidiomycetes									
Order: Aphyllophorales									
Family: Steraceae									
Thelephora terrestris	15.9	49.0	49.0	8.0	<0.1	<0.1	<0.1	<0.1	<0.1
Family: Clavariaceae									
Ramaria pallida	3.7	3.0	3.0	2.0	3.0		81.0	13.0	
Sparassis crispa (1)	1.03	<0.1	Trace	<0.1	Trace	Trace	31.0	66.0	<0.1
Sparassis crispa (2)	0.57	Trace	Trace	<0.1	Trace	Trace	Trace	45.0	45.0
Family: Cantharellaceae									
Gomphus clavatus	4.47	<0.1	Trace	Trace	2.0	1.0	87.0	8.0	1.0
Order: Agaricales									
Family: Polyporaceae									
Albatrellus cristatus	7.72	<0.1	<0.1	<0.1	1.0	1.0	91.0	2.0	<0.1
Albatrellus ovinus	0.24	12.0	24.0	Trace	Trace	Trace	64.0	Trace	<0.1
Albatrellus pescaprae	0.77	Trace	<0.1	Trace	<0.1	<0.1	94.0	<0.1	<0.1
Family: Tricholomataceae									
Laccaria fraterna (1)	11.2	7.0	93.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Laccaria fraterna (2)	30.0	6.0	94.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Laccaria laccata var. *pallidifolia* (1)	0.66	Trace	45.0	Trace	55.0	<0.1	<0.1	<0.1	<0.1
Laccaria laccata var. *pallidifolia* (2)	4.26	2.0	1.0	Trace	88.0	<0.1	9.0	<0.1	<0.1
Lyophyllum conglobatum	0.63	<0.1	Trace	<0.1	34.0	<0.1	66.0	<0.1	<0.1
Tricholoma inamoenum	0.39	Trace	<0.1	Trace	100.0	<0.1	<0.1	<0.1	<0.1
Tricholoma pardinum	0.63	11.0	5.0	<0.1	21.0	<0.1	63.0	<0.1	<0.1
Tricholoma sulphureum	0.26	72.0	Trace	<0.1	28.0	<0.1	<0.1	<0.1	<0.1
Family: Pluteaceae									
Volvariella volvacea (1)	0.82	Trace	4.0	8.0	78.0	<0.1	10.0	<0.1	<0.1
Volvariella volvacea (2)	1.05	Trace	6.0	Trace	94.0	<0.1	Trace	<0.1	<0.1
Family: Entolomataceae									
Entoloma rhodopolium	0.55	28.0	55.0	<0.1	17.0	<0.1	<0.1	<0.1	<0.1
Family: Lepiotaceae									
Macrolepiota procera	0.42	Trace	Trace	Trace	Trace	<0.1	100.0	<0.1	<0.1
Leucocoprinus badhamii	2.9	Trace	2.0	Trace	47.0	Trace	49.0	Trace	1.0
Family: Agaricaceae									
Agaricus abruptibulbus	3.49	1.0	3.0	5.0	3.0	<0.1	88.0	<0.1	<0.1
Agaricus bisporus	1.0	<0.1	12.0	6.0	27.0	<0.1	55.0	<0.1	<0.1
Agaricus campester	1.32	Trace	<0.1	Trace	Trace	4.0	96.0	<0.1	<0.1
Agaricus elvensis	2.43	2.0	4.0	2.0	4.0	<0.1	84.0	<0.1	4.0
Agaricus fuscofibrillosus	2.54	Trace	1.0	<0.1	4.0	<0.1	95.0	<0.1	<0.1
Agaricus lilaceps	1.78	6.0	3.0	<0.1	24.0	<0.1	66.0	<0.1	1.0
Agaricus macrosporus	3.32	<0.1	3.0	4.0	8.0	<0.1	85.0	<0.1	<0.1
Agaricus silvicola	6.24	1.0	3.0	<0.1	4.0	<0.1	90.0	<0.1	2.0
Agaricus subrutilescens	10.8	0.5	1.0	1.0	1.5	<0.1	96.0	<0.1	<0.1
Family: Amanitaceae									
Amanita phalloides	0.55	Trace	Trace	Trace	Trace	<0.1	Trace	<0.1	<0.1
Amanita magniverrucata	0.50	Trace	Trace	Trace	Trace	<0.1	<0.1	<0.1	<0.1
Amanita muscaria	3.11	13.0	3.0	<0.1	6.0	72.0	2.0	2.0	1.0
Amanita caesarea	0.45	32.0	38.0	<0.1	13.0	<0.1	<0.1	17.0	<0.1
Amanita rubescens	0.12	Trace	<0.1	<0.1	Trace	<0.1	<0.1	<0.1	<0.1
Order: Gastrales									
Family: Lycoperdaceae									
Calvatia excipuliformis	0.72	4.0	4.0	<0.1	20.0	<0.1	72.0	<0.1	<0.1
Calvatia utriformis	0.79	Trace	6.0	<0.1	9.0	<0.1	85.0	<0.1	<0.1
Lycoperdon echinatum	1.23	Trace	10.0	<0.1	12.0	<0.1	78.0	<0.1	<0.1
Lycoperdon perlatum	2.81	Trace	Trace	7.0	5.0	<0.1	88.0	<0.1	<0.1
Lycoperdon piriforme	0.46	8.0	30.0	Trace	Trace	<0.1	62.0	<0.1	<0.1
Geastrum sp.	3.12	2.0	2.0	Trace	2.0	<0.1	94.0	<0.1	<0.1

Numbers in the column heads are as indicated in Fig. 3.

Table 2
Distribution of arsenic in leaves of plants collected from As-contaminated areas in Ron Phibunand and Bannang Sata ($\mu g\,g^{-1}$ DW) [48]

Plant family	Scientific name	Type	Ron Phibunand	Bannang Sata
Acanthaceae	*Pseuderanthemun* sp.	Herb	39.0	NC
Araceae	*Colocasia esculenta*	Herb	19.0	NC
Asteraceae	*Ageratum coconyzoides*	Herb	35.0	20.0–28.0
Blechnaceae	*Blechnum orietate*	Fern	5.0–24.0	NC
Caesalpinioideae	*Bauhinia glauca*	Tree	15.0	29.0–61.0
	Bauhinia acuminata	Tree	12.0–15.0	NC
Compositae	*Pluchea torvum*	Shrub	65.0	80.0
Cyperaceae	*Cyperus* spp.	Herb	24.0–40.0	25.0–39.0
Euphorbiaceae	*Euphorbia* sp.	Herb	12.0	NC
	Mallotus floribundus	Tree	10.0	NC
Gleicheniaceae	*Dicranopteris linearis*	Fern	32.0	51.0–77.0
Gramineae	*Panicum repens*	Grass	40.0	NC
	Paspalum sp.	Grass	27.0	NC
Marantaceae	*Maranta* sp.	Herb	21.0	NC
Melastomalaceae	*Melastoma malabathricum*	Shrub	14.0–16.0	18.0–37.0
Mimosaceae	*Mimosa invisa* var. *invisa*	Herb	NC	24.0–51.0
	Mimosa pudica var. *unijuga*	Herb	41.0–55.0	48.0–76.0
Moraceae	*Ficus* sp.	Tree	4.0	NC
Musaceae	*Musa acuminata*	Herb	23.0	35.0
	Musa sp.	Herb	NC	18.0
Papilionaceae	*Crotalaria pallida*	Shrub	NC	6.5
Papilionoideae	*Centrosema oubescens*	Climber	31.0	34.0–54.0
Parkeriaceae	*Pityrogramma calomelanos*	Fern	3860–6380	2270–4030
Poaceae	*Eleusine indica*	Grass	6.0–8.0	NC
	Imperata cylindrical	Grass	25.0	23.0
Pteridaceae	*Pteris vittata*	Fern	4240–6030	NC
Rosaceae	*Rubus* sp.	Shrub	23.0	NC
Selaginellaceae	*Selaginella* spp.	Climber	30.0–48.0	21.0
Schizaeaceae	*Lygodium polystachyum*	Fern	10.0–14.0	NC
Scrophulariaceae	*Scoparia dulcis*	Herb	25.0–42.0	NC
Sterculeaceae	*Helicteres hirsuta*	Shrub	26.0	NC
Solanaceae	*Solanum trovum*	Shrub	1.2	NC
Thelypteridaceae	*Thelypteris* sp.	Fern	2.0	NC
Typhaceae	*Typha angustifolia*	Herb	NC	5.0
Verbenaceae	*Stahytarpheta urticaefolia*	Herb	0.4–0.6	NC
Ulmaceae	*Trema orientalis*	Tree	6.0–30.0	10.0

NC: Not collected.

60% water-extractable, 95% of which was present as arsenate. In contrast, arsenic in the fern fronds was readily extracted into water (86–93%) and was present mainly as arsenite (60–72%) with the remainder being arsenate. Methylarsonate and dimethylarsinate were detected as trace constituents in only two fern samples. The concentration of inorganic and organic arsenic have been determined in leaves of different plants collected in same Ron Phibun and Bannang Sata districts, Thailand [48] (Table 2). High level of total arsenic was found in two additional fern species: *Pityrogramma calomelanos* and *Pteris vittata* (up to 6400 $\mu g\,g^{-1}$). The ability of *Pityrogramma calomelanos*, *Pityrogramma calomelanos* and *Pteris vittata* to withstand the very high concentrations of arsenic in soil suggests that these plants have a mechanism to detoxify of the inorganic arsenic. Mechanisms of arsenate tolerance have been illustrated in some plant species, e.g. *Holcus lanatus* [49], *Agrostis capillaries* and *Deschampsia cespitosa* [50] and *Silene vulgaris* [51]. Arsenate behaves as a phosphate analogue [52,53]and is taken up by the phosphate transport system. In these arsenate tolerant plants, the phosphate uptake system was suppressed which led to reduced influx of arsenate into the plants.

Since the ferns *Pityrogramma calomelanos*, *Pityrogramma calomelanos* and *Pteris vittata* are both As-tolerant and As-hyperaccumulators, the mechanism of As resistance may rely on the ability of the plant to detoxify and/or biotransforming toxic As to lipid- and/or water-soluble arsenic species [47]. Hyperaccumulation and engineering tolerance of arsenic in plants by combining arsenate reductase and γ-glutamylcysteine synthetase expression has recently been reported [54]. By expressing bacterial genes encoding these enzymes in Arabidopsis, the oxyanion arsenate was transported aboveground, reduced to arsenite, and sequestered in thiol-peptide complexes in the plants [54].

Arsenic species such as As(III), As(V), MMA, DMA also have been found in many cultivated vegetables and fruits: garlic, onion, potato, carrot, beetroot, spinach, asparagus, cabbage, rice, radish, chard, corn, tomato, beans, and concentration of these arsenic species can be varying

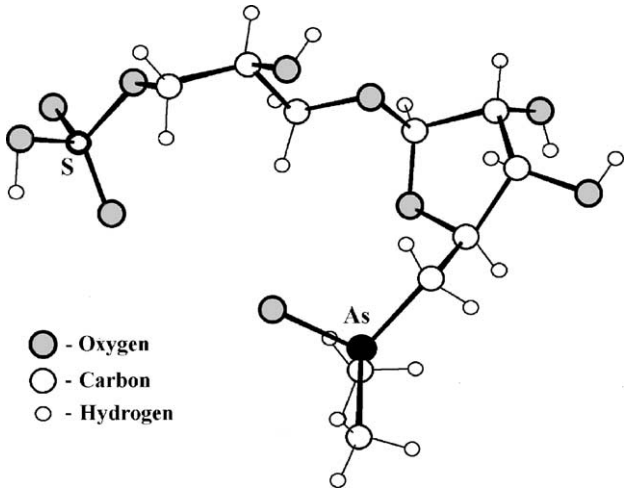

Fig. 4. Crystal structure of organoarsenic compound, sulfate-ribose (**15**), isolated from plants, lichens, fungi and algal species. Adapted by authors.

from locations where vegetables and fruits were collected ([10,55,56], and references cited). Crystal structure of sulfate-ribose (**15**), isolated from plants and algal species show in Fig. 4.

4. Occurrence of arseno compounds in freshwater and marine algal species

Marine algae synthesized many different biological active compounds [57–61], produced boron-containing [15,16] and organoarsenic compounds [11,12,62,63]. In 1922 Jones [64] first reported high concentrations of arsenic in marine algae collected from the British coast. The author examined algae such as *Fucus* spp. and *Chondrus crispa* (Irish moss) that were traditionally used for pharmaceutical purposes or as food. The presence of arsenic in lipid-soluble fraction of marine oils was first recognized by Vinogradov [65]. These early studies on the characterization of arsenic in algae were chiefly concerned with the proportions of organically bound and inorganic arsenic species and/or the relative contributions of water-soluble and lipid-soluble arsenic compounds. The distribution of arsenic species in lipids of the different marine organisms has been demonstrated in extensively works by Lunde [66–69]. He analyzed several cultured in laboratory freshwater and marine algae and detected very low (0.5–4.8 ppm) arsenic concentrations in the lipid extracts [70].

Two groups of scientists have studied the distribution of arsenic species in marine brown algae *Hizikia fusiforme*

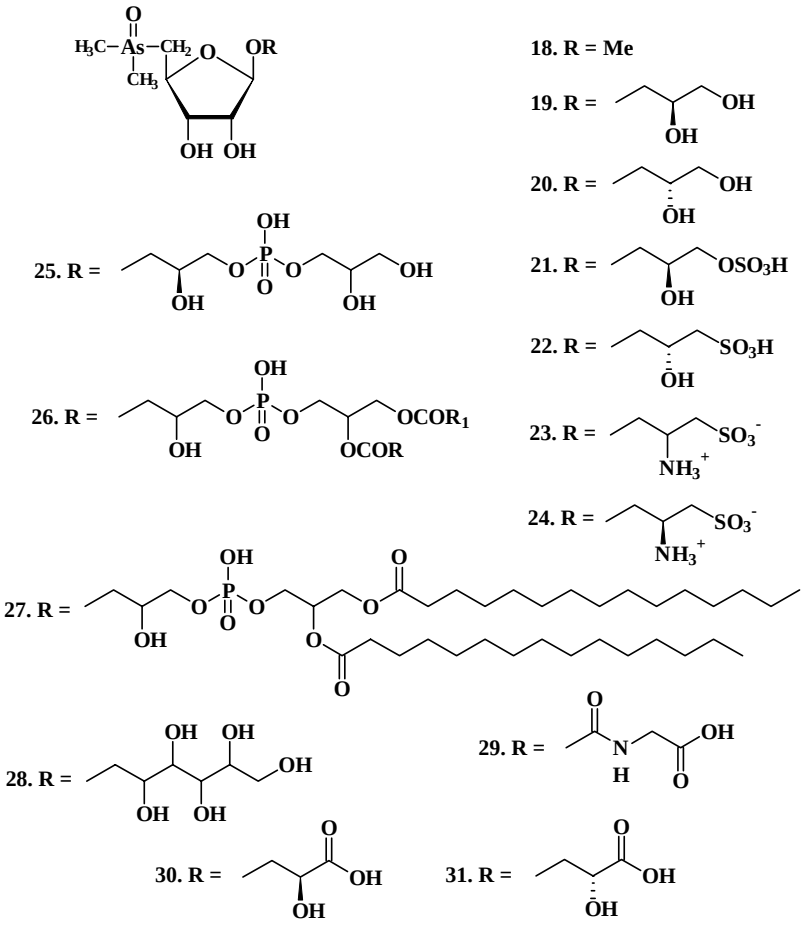

Fig. 5. Organoarsenic species isolated from freshwater and marine algal species.

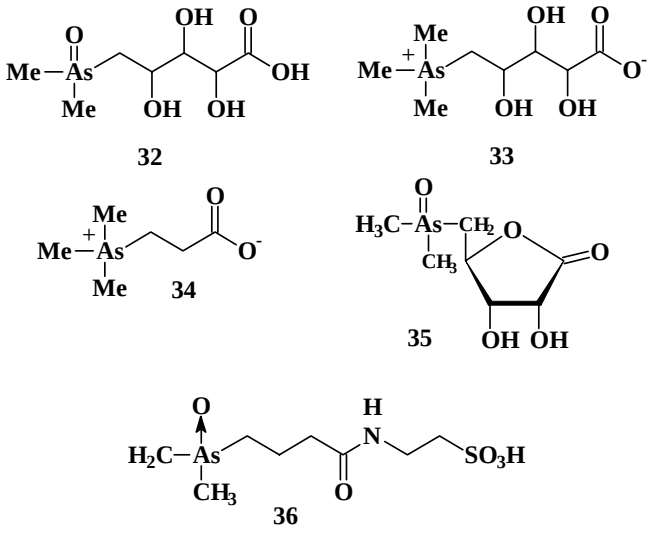

Fig. 6. Novel organoarsenic species were found in Sargassaceae family.

(phylum Sargassaceae) [71–73]. Aqueous extracts of *Hizika* contained methylarsonic acid **7** and dimethylarsinic acid **8** in addition to inorganic arsenic and other unknown organic compounds. Recent investigation of the *Hizikia* species showed that these algae contain another arsenosugars such as (No. **15**–**17** in Fig. 3; No. **19**,**23** in Fig. 5) [21].

Other members of the Sargassaceae family produced similar results. Studies of similar type directed at *Laminaria japonica* [62] and *Laminaria digitata* [74] indicated that arsenic species were present as (**1**–**5**,**8**,**12**–**17**), as well as some novel arseno compounds (No. **32**–**35** in Fig. 6). Four organoarsenic species (**14**–**17**) have been isolated from *Laminaria* sp. [29]. *Sargassum lacerifolium* is one more representative member of the family Sargassaceae that has analyzed for the presence of arsenic species [20,75]. Arsenomethionine (No. **36** in Fig. 6) and two diastereoisomers (**41**a and **41**b in Fig. 7) of (**41**) were found as major compounds in *Sargassum lacerifolium* [75].

The polar parts of compounds (**41** and **41**a,b) are similar to of non-phosphorus-containing betaine lipids such as DGTS (diacylglyceryl-O-4′-(*N*,*N*,*N*-trimethyl)-homoserine) (No. **43** in Fig. 8) and DGTA (dicaylglyceryl-O-2′-(hydroxylmethyl)-(*N*,*N*,*N*-trimethyl)-β-alanine) (**44** in Fig. 8). These polar betaine lipids are an important and major membrane component of freshwater, brackish and marine algal species [57,76–78], lichens [79–81], fungi [82,83], as well as some vascular plants [82,84–86]. Lipids (**43**) and (**44**) have trimethylammnio group, and (**41**a,b) have an arseno group that carries two methyls and 5′-deoxyribos-5-yl group as substituents. This last group is related to the major dimethylarsinoylribose derivatives of *Sargassum lacerifolium*. The similarities between compounds (**41**a,b) and (**44**) suggest a parallel biosynthetic processes (see Fig. 8) [75].

Arsenic-containing ribofuranosides (**14**–**17**) as well as inorganic (**10**–**12**) compounds have been isolated from collected freshly samples at the Australian brown kelp *Ecklonia*

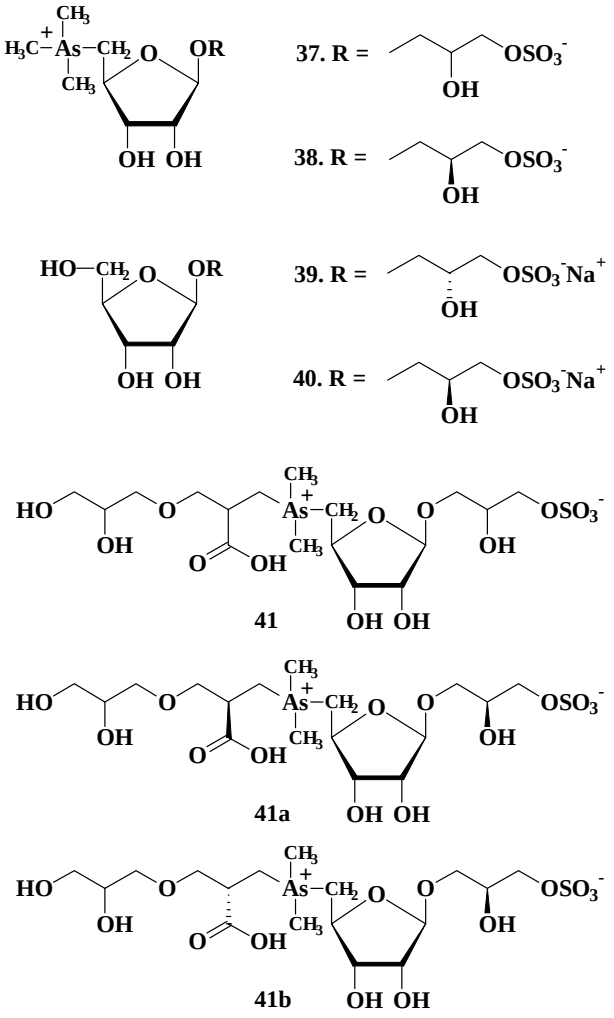

Fig. 7. Arsenosugars isolated from marine algal species.

radiana [87]. Different organoarsenic compounds have also been isolated from other brown *Laminaria japonica*, *Sphaerotrichia divaricata*, *Undaria pinnatifida*, *Sargassum lacerifolium*; green alga *Codium fragile*, and red alga *Porphyra tenera* [62], which collected from the Japanese and Australian coasts. Recently, Tukai et al. [88] has been studied in the distribution of arsenoribosides and inorganic arsenic compounds in three classes of marine algae: Phaeophyta (brown), *Echlonia radiata*, *Padina fraseri*, *Lobophora* sp., *Hormosira bankii*, *Sargassum* sp.; Rhodophyta (red), *Corallina officinalis*, *Amphiroa anceps*, *Laurencia* sp.; and Chlorophyta (green), *Cladophora subsimplex*, *Codium lucasii*, *Ulva lactuca* collected from the coastline near Sydney (Australia). The authors isolated three major arsenoribosides (**15**–**17**) from all examined samples.

Geiszinger et al. [16] investigated the transformation of inorganic arsenate during 19 weeks in the brown alga *Fucus serratus*. The authors found that the alga readily accumulated arsenate and transformed it into several arsenic compounds, depending on the exposure concentration in seawater. Biotransformation of arsenic by *Fucus* was monitored by HPLC

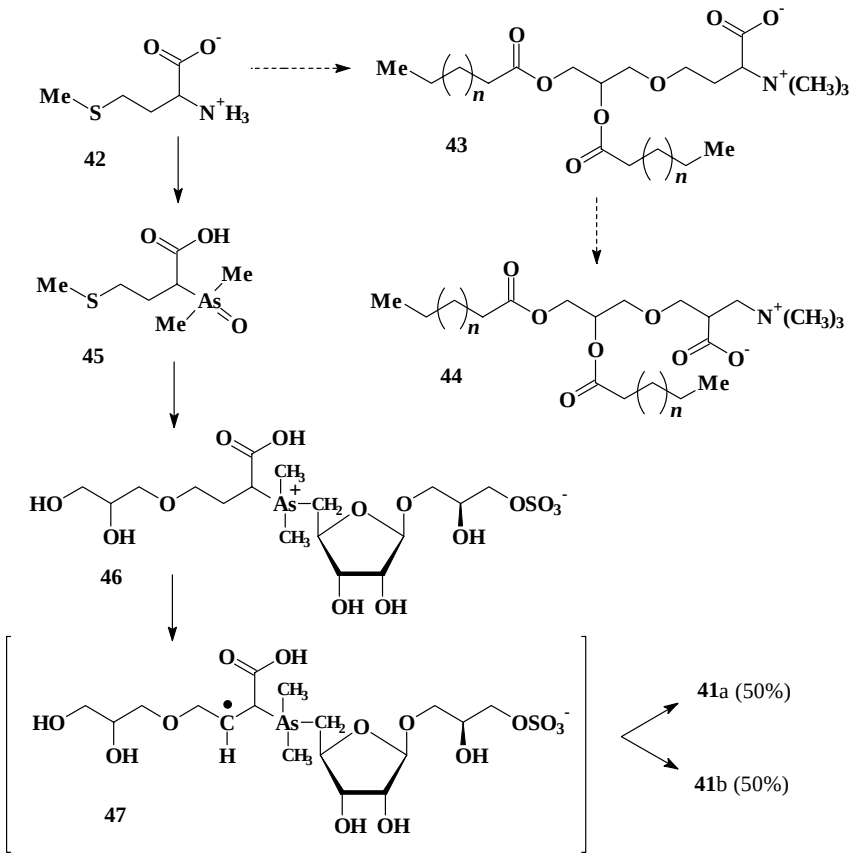

Fig. 8. Possible biotransformation some organoarsenic compounds via arsenomethionine and betaine lipids in *Sargassum* algal species [75]. Adapted by authors.

analysis, and arsenite, arsenate, MMA, DMA, and arsenosugars (**14**–**17**) were found. Based on these experimental results authors concluded that transformation of inorganic arsenic into various arsenosugars via the formation of an intermediate N-[4-(dimethylarsinoyl)butanoyl]taurine (**36**) and/or nulceoside (**48**), as shown on Fig. 9. Fungus *Fusarium oxysporum melonis* which an associated and isolated from marine alga *Fucus gardneri* [89] also accumulated and transformed arsenic to mutilated compounds.

In some studies attempted to further characterization of the arsenic compounds elaborated by algae [90]. These studies have, with one exception, involved the growth of algae (usually phytoplankton) in media containing radiolabelled arsenate. A study [91] of arsenic accumulated in the polar lipid (phospholipid) fraction of extracts from the microalga *Tetraselmis chuii* followed large-scale production of the alga in a medium enriched in unlabelled arsenate. Examination by thin-layer chromatography revealed an arsenic compound migrating with phosphatidylethanolamine. Hydrolysis of this product with phospholipase led the authors to speculate that there might have been an arsenocholine moiety in the lipid. This tentative conclusion seemed unlikely in the light of work published [92] one year later examining the products of phyloplankton (*Chaetoceros concavicornis*) subjected to radiolabelled arsenate. The authors claimed to have identified an arsenolipid in extracts of the alga that was based on the presence of trimethylarsoniolactate, i.e. trimethylarsoniolactate substituted for choline in, for example, lecithin [93]. Their identification was based upon chromatographic and electrophoretic coordinates and a comparison of these with trimethylarsonolactate, apparently obtained by synthesis. The results were particularly conclusive as the authors claimed to be able to convert their compound to arsenobetaine by simple chemical reactions.

The unicellular microalgae such as *Chladomydomonas reihardtii* [94] and *Polyphysa peniculus* [95] as well as green algae *Chlorella* sp. [96], *Chlorella vulgaris* [97], and *Phormidium* sp. [98] can be accumulate and biotransforming inorganic arsenic to methylated species. Another marine microalgae, such as *Dunaliella salina*, *Chattonella antiqua*, *Heterosigma akashimo*, *Skeletonema costatum*, *Chaetoceros debile*, and *Thalassiosira weissflogii* [99], are tolerant to arsenate and accumulate As(III) and As(V) in high concentrations, and can to transform (**1**) and (**2**) to other arsenic species MMA, DMA, and TMA. The synthesis of both lipid-soluble and water soluble arsenic compounds has been demonstrated in two green algae *Chlorella ovalis*, *Ch. pyrenoides*, cyanobacterium *Oscillatoria rubenscence*, and two diatoms *Phaeodactylum tricolor* and *Skeletonela costatum* [100]. Radioautography on TLC shown

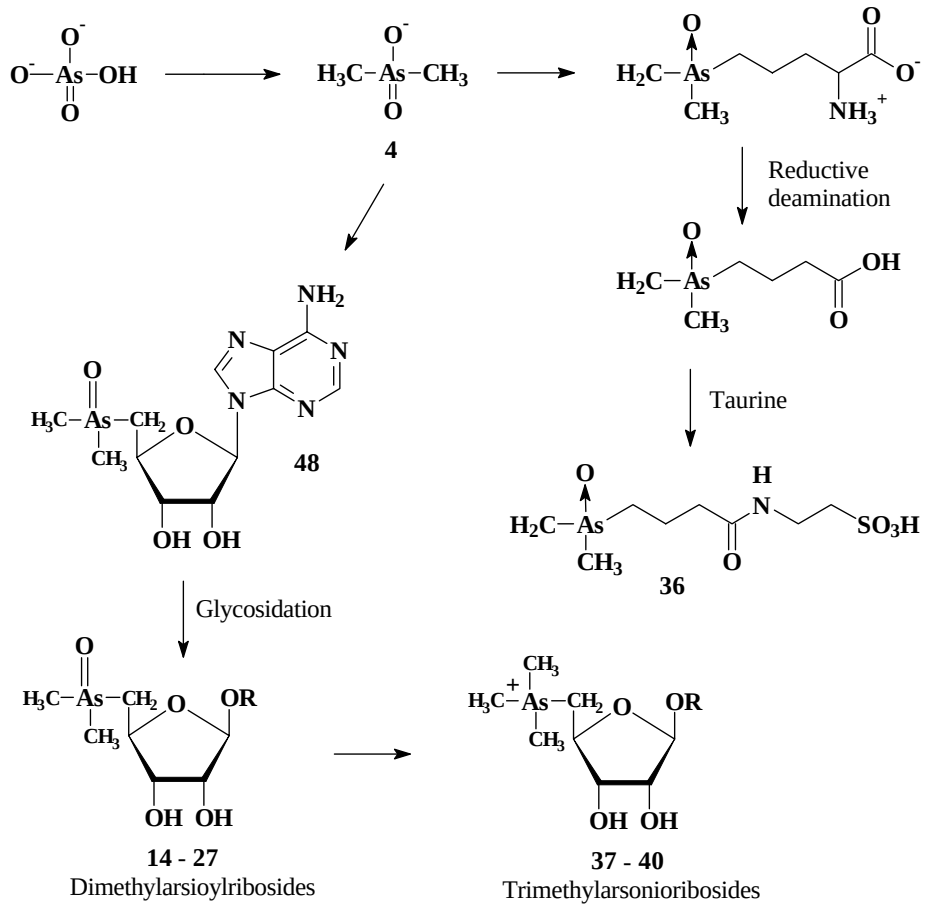

Fig. 9. Proposed biogenic pathway for major arsenosugars found in marine algae [62,88]. Adapted by authors.

that radioactive As the presence among polar lipids in all examined species.

5. Microbial conversion of arsenic to methylated arsenic species

The term biological methylation refers to as enzymatic transfer of a previously formed methyl group from donor atom to acceptor atom within a living organisms. Enzymes involved in such transformation have term methyltransferases and they are well known in nature [101,102]. Since microbial methylation of arsenic has been recently reviewed [103–105], this topic will not be considered here in depth.

More than 60 years ago Challenger group was reported that *Penicillium chrysogenum* and strains of *Penicillium notatum*, *Aspergillus niger*, and *A. fischeri* did not methylate arsenous acid in the usual bread crumb cultures [101,106–108]. *A.glaucus* and *Aspergillus versicolor* formed trimethylarsine to a limited extent. However, all of these organisms converted methylarsonate into trimethylarsine. Trimethylarsine was formed from dimethylarsinate by *P.notatum*, *P. chrysogenum*, and also two strains of *A.niger*. The latter microorganism converted ethylarsonate to dimethylethylarsine and *P.chrysogenum* converted allyllarsonate to dimethylallylarsine. Two organisms, *Gliocladium roseum* and a *Penicillium* species, converted methylarsonate and dimethylarsinate to trimethylarsine under a range of culture conditions; however, neither arsenate nor arsenite was volatilized. The variables affecting the methylation of arsenic by yeast *Cryptococcus humiculus* have been studied [1,109]. All of the organic As(V) compounds of the Challenger pathway (methylarsonate, dimethylarsinate, trimethylarsine oxide) have been observed in cell extracts which metabolizing arsenate, and all of them are precursors for trimethylarsine biosynthesis [110,111]. The preconditioning of cells with dimethylarsinate improves the formation of trimethylarsine from arsenate and dimethylarsinate. In later experiments, the nonvolatile components of *C.humiculus* and *Scopulariopsis brevicaulis* were also identified [112]. Three soil bacterial samples were incubated with arsenate, arsenite, methylarsonate, and dimethylarsinate, methyl- and dimethylarsine were only produced from methylarsonate and dimethylarsinate. Surprisingly, two soil bacteria (a *Pseudomonas* sp. and an *Alcaligenes* sp.) produced only arsine when incubated anaerobically with arsenate or arsenite [113].

Some bacterial species, such as *Corynebacterium* sp., *E.coli*, *Flavobacterium* sp., *Proteus* sp., and *Pseudomonas* sp., that were isolated from the environment and acclimatized to growth in the presence of sodium arsenate, transformed arsenate to arsenite, and all microorganisms produced dimethylarsine. In addition *Pseudomonas* sp. formed all three of the methylated arsines [114]. Another bacterial species such as *Achromobacter* sp., *Aeromonas* sp., *Alcaligenes* sp., *Flavobacterium* sp., *Nocardia* sp., and *Pseudomonas* sp. produced both mono- and dimethylarsine from methylarsonate but only two of them produced trimethylarsine, and a *Nocardia* sp. was the only organism that produced all of the methylarsines from this substrate [115]. Arsenic-resistant *Pseudomonas putida*, isolated from a contaminated *Chlorella* culture, contained a nonvolatile trimethylarsenic species and all three methylated species were excreted into the medium [116]. Similar results were obtained with arsenic-resistant *Klebsiella oxytoca* and a *Xanthomonas* sp. [117]. A sample of soil with a low level of arsenic contamination (As, 1.5 ppm) yielded two arsenic-resistant, non-methylating bacteria (*Bacillus* sp. and *Pseudomonas fluorescens*) and a new, arsenic-resistant organism, assigned to the *Flavobacterium-Cytophaga* groups, with methylating capacity. It produced only trimethylarsine as the volatile material, but arsenite was transformed more rapidly than arsenate, and dimethylarsinate did not yield trimethylarsine [118].

The microorganisms from particles collected in the deep sea, between 1100 and 3500 m in depth, and showed decomposing ability [119]. With the particles from 1100 m, the degradation products were the same as those produced by microorganisms occurring in sources in the photo active zone, i.e. trimethylarsine oxide, dimethylarsinic acid and inorganic As(V). At 3500 m, the degradation activity was diminished, with smalls amount of DMA and TMAO being produced. These results suggest that arsenobetaine contained in the marine algae, as well as in invertebrates starts to degrade immediately after the death of marine invertebrates and algae and their transformation to particles. The degradation of arsenobetaine to inorganic arsenic in tentative arsenic cycle in marine ecosystems (inorganic arsenic to inorganic arsenic via the biosynthesis of arsenobetaine) may apply to the deep sea as well as to the photic zone. Authors concluded that the arsenobetaine-decomposing ability of microorganisms occurring in sinking particles, which play a main role in the vertical transport of organic substances produced in the photosynthetical active zone [119].

Five species of the halophyte archebacterial species *Artrochnemum perenne*, *Artrochnemum fruticosum*, *Spartina maritima*, *Halimione portulacoides* and *Halimione* spp. were collected at the Pancas salt-marsh study site within the Tagus Nature Reserve, Portugal, and cultivated in the laboratory [120]. A high content of arsenic was found in the samples of halophytes studied, both di- and trimethylated arsenic and arsenobetaine and arsenocholine compounds being present. In addition, the latter hyphenated technique

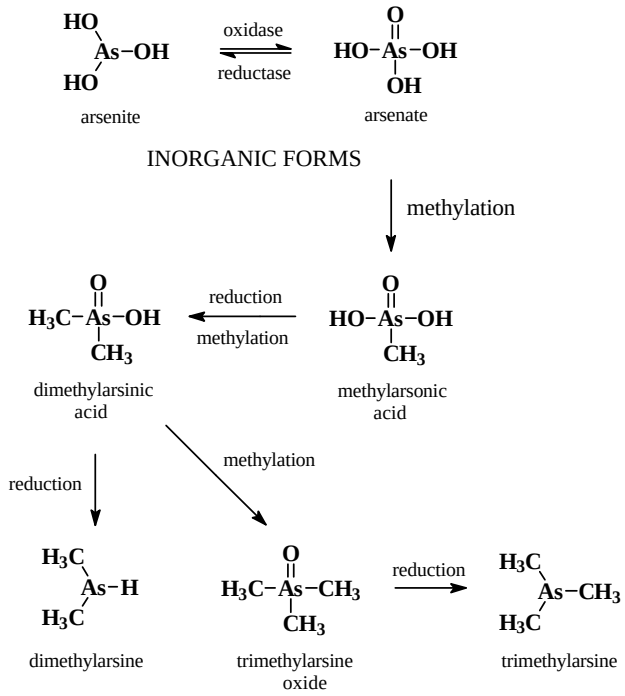

Fig. 10. Microbial formation of methylated organoarsenic compounds from inorganic arsenate [103,105]. Adapted by authors.

strongly suggests the presence of a number of other organoarsenicals including tetramethylarsonium, trimethylarsine oxide, cacodylate (DMA) and several unidentified an arsenosugar type compounds. This is the first report that the bacterial species could be producing water- and lipid soluble arseno-containing species.

Obtained a numerous studies of microorganisms [101–105], it should be concluded that the conversion of water-soluble arsenate to volatile trimethylarsine is a multistep process (see Fig. 10), with arsenate initially being reduced to arsenite. There then follows a sequence of methylation and reoxidation, followed by the reduction of the organoarsenical intermediates. Dimethylarsinic acid is the substrate for microbial conversion to the arsenobetaine and arsenolipids found in freshwater and marine algal species and invertebrates [11–14].

The naturally accruing organoarsenic species have been found in representatives of all main taxonomic groups: plants, fungi, lichens, micro- and macro- algal species, and microorganisms. It is probably too early to say whether the nature of arsenic compounds, and use them for any chaemotaxonomic significance, in general, and/or for each taxonomic group in particular.

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