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Review

Biologically active compounds of semi-metals

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Abstract

Semi-metals (boron, silicon, arsenic and selenium) form organo-metal compounds, some of which are found in nature and affect the physiology of living organisms. They include, e.g., the boron-containing antibiotics aplasmomycin, borophycin, boromycin, and tartrolon or the silicon compounds present in ''silicate'' bacteria, relatives of the genus *Bacillus*, which release silicon from aluminosilicates through the secretion of organic acids. Arsenic is incorporated into arsenosugars and arsenobetaines by marine algae and invertebrates, and fungi and bacteria can produce volatile methylated arsenic compounds. Some prokaryotes can use arsenate as a terminal electron acceptor while others can utilize arsenite as an electron donor to generate energy. Selenium is incorporated into selenocysteine that is found in some proteins. Biomethylation of selenide produces methylselenide and dimethylselenide. Selenium analogues of amino acids, antitumor, antibacterial, antifungal, antiviral, anti-infective drugs are often used as analogues of important pharmacological sulfur compounds. Other metalloids, i.e. the rare and toxic tellurium and the radioactive short-lived astatine, have no biological significance.

Keywords: Semi-metals; Boron; Silicon; Arsenic; Selenium; Organometallic compounds; Bacteria; Fungi; Higher plants

Contents

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1. Introduction

In the periodic table of elements, semi-metals (metalloids) are found along the line that distinguishes metals from nonmetals. Together with metals and nonmetals, metalloids form one of the three categories of chemical elements as classified by ionization and bonding properties (Rochow, 1966; Venugopal and Luckey, 1978). They have some of the qualities of both metals and nonmetals. Unlike the true metals, metalloids are usually semiconductors rather than conductors and have therefore received intensive attention from the computer and electronics industries. Their relative abundance in the environment is summarized in Table 1.

When involved in chemical bonding, the metalloids again exhibit intermediate qualities. They are capable of taking electrons from most metals and will readily lose electrons to most nonmetals. Their electronegativity values are also mid-range. They usually establish covalent bonding, ionic bonding being rather rare.

The reactivity of the metalloids depends on the counter-element. Boron acts as a nonmetal when reacting with sodium yet as a metal when reacting with fluorine. In organic compounds, they can substitute other elements such as sulfur. Boron and arsenic form compounds with lipids, sugars, phenols, organic acids and some polymers. Organic arsenic compounds are components of the food chains of many organisms including humans and may play important biological roles in them. Selenium is found in living organisms in its soluble inorganic forms and as protein-bound and free seleno-amino acids and volatile organoselenium compounds. Most small organic selenium compounds in living cells are isologues of sulfur amino acids or their derivatives. The interactions of silicon with living matter are vitally important for some bacteria, which release silicon from aluminosilicates through the secretion of organic acids, or for unicellular algae – diatoms for which it serves as the basic building block of their bodies. Tellurium is highly toxic and is not thought to be required by biological systems; the highly radioactive astatine is so rare in nature that the existence of biological astatine compounds is highly improbable.

Table 1
Relative abundance of metalloids in the environment

Element	In Earth's crust (mg/kg)	In sea water (mg/L)
As	1.8–5.0	0.003
B	3–10	4.6
Se	0.05–0.09	0.00009
Si	257,000–282,000	3
Te	0.001–0.005	0
At	0	0

2. Boron

Boron is a ubiquitous element in rocks, soil, and water, its average concentration ranging from ~1 mg/kg in fresh water to ~100 mg/kg in rocks (Steinberg, 1964).

Tetrahedral borate or boronate complexes have been shown to be involved in enzyme inhibition. Serine proteases were proposed to be inhibited by boric acid (Antonov et al., 1968), and simple borates have been patented as protease stabilizers in liquid detergent formulations (Hora and Kivits, 1981; Severson, 1985).

Serine hydrolase enzymes react with various borates, boronates, and borinates by forming a tetrahedral complex between the serine hydroxyl group and the boron atom. Hydrogen bonding to the imidazole ring of an adjacent histidine adds further stabilization (Fig. 1). Boric acid forms complexes with sugars, phenols, organic acids, and some polymers (Boesekem, 1949; Raven, 1980).

2.1. Boron in bacteria

In bacteria boron is an essential part of signal molecules required for quorum sensing (Goldbach and Wimmer, 2007). For instance, an AI-2 furanosyl borate diester complex (**1**) that was identified in the bioluminescent marine bacterium *Vibrio harveyi* as one of two autoinducers that regulate light production in response to cell density (Bassler et al., 1993, 1994; Cornell et al., 1996; Della Ragione et al., 1985) has been proposed to serve as a "universal" bacterial quorum-sensing boron-containing signal for

inter-bacterial community communication (Chen et al., 2002).

A tripeptide substrate-like boronic acid inhibitor was used to elucidate the crystal structure of *Escherichia coli*

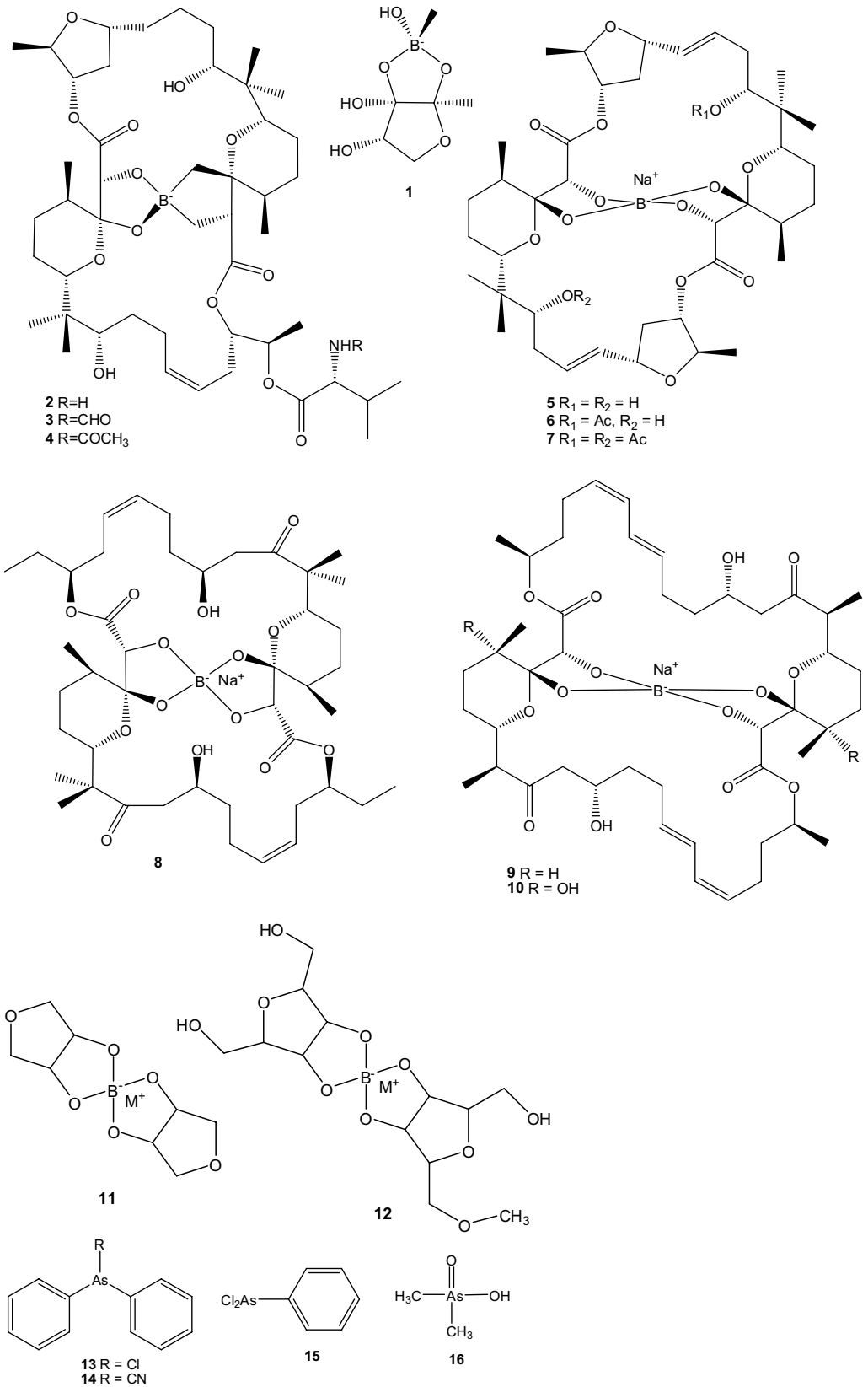
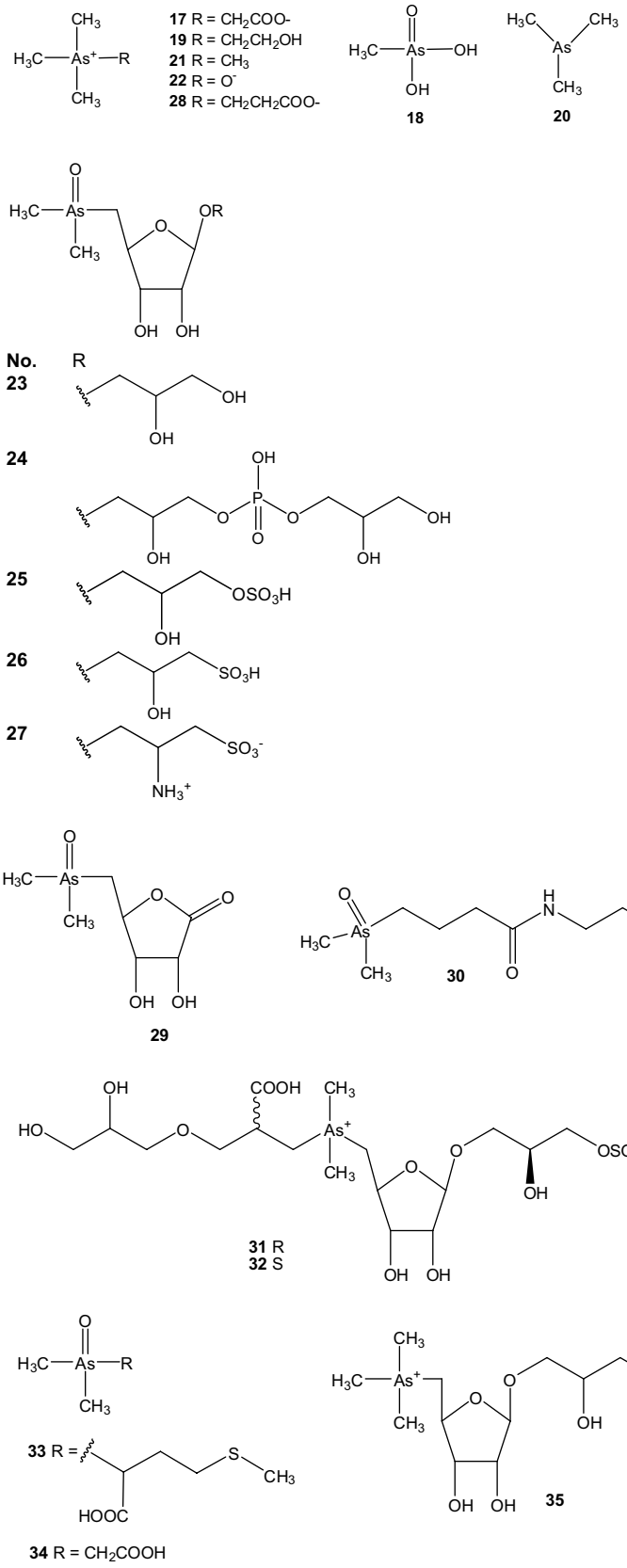


Fig. 1. Complex formation between a peptide and boron atom.



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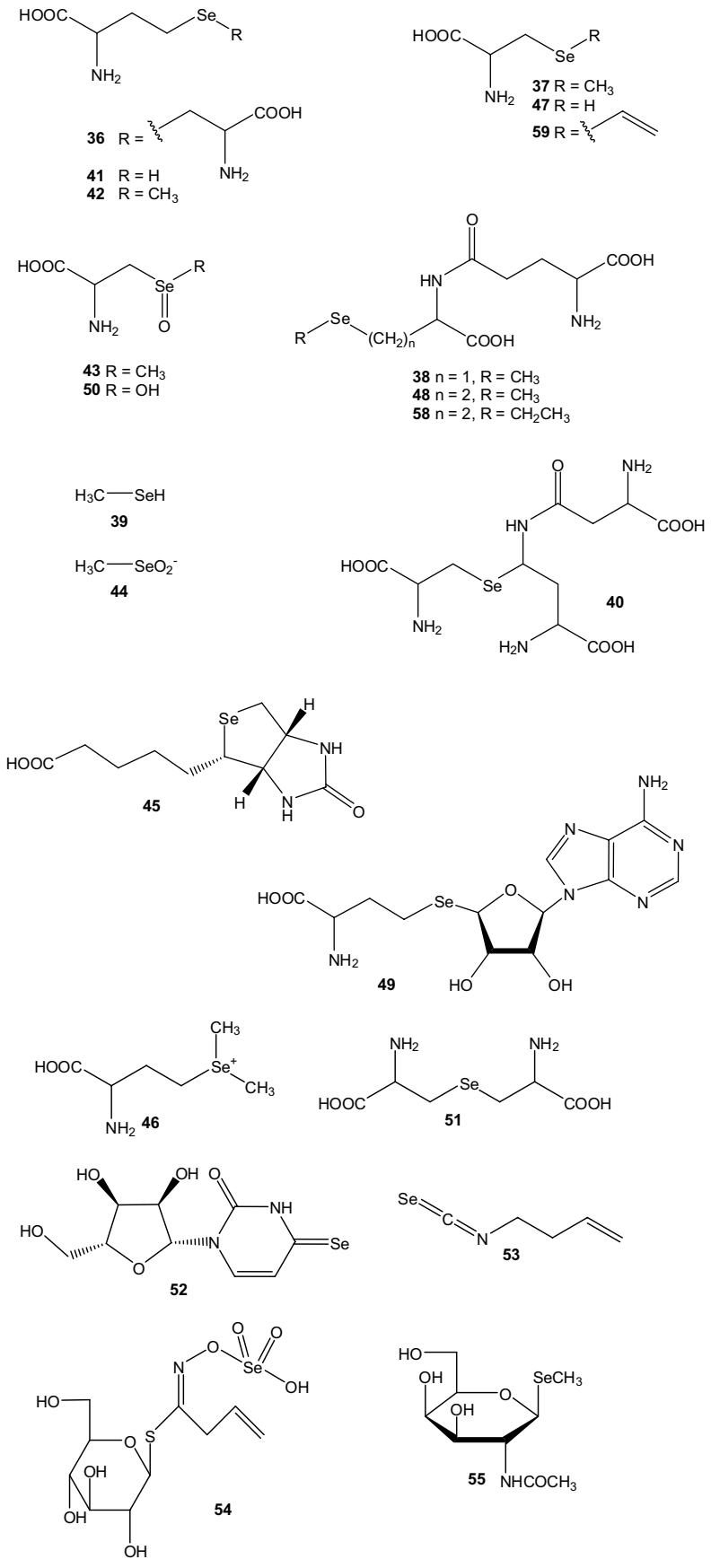

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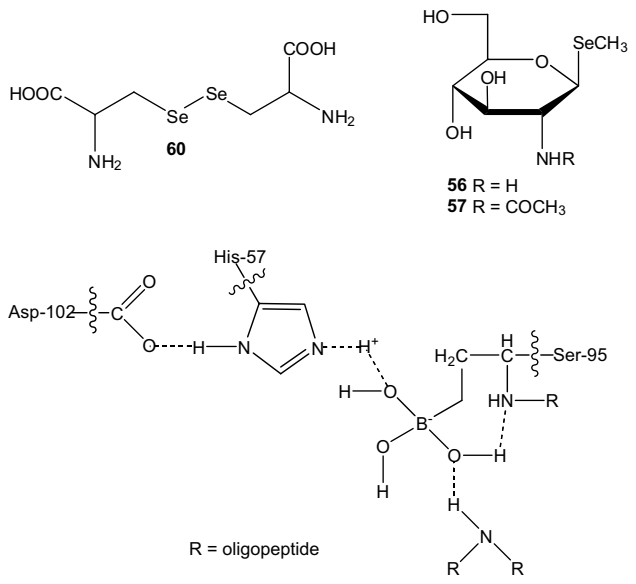

Fig. 1 (*continued*)

D-alanine carboxypeptidase–penicillin-binding protein 5 (PBP 5) (Nicola et al., 2005). PBP 5 forms a peptide boronic acid complex resembling the transition-state intermediate during the deacylation step of the enzyme-catalyzed reaction with peptide substrates. The use of the peptide contributed to elucidating the structure of the complex. Boron-containing compounds called borinic esters, with broad antibacterial activity (MIC in the low micrograms/millilitres range) were found to inhibit two essential bacterial enzymes, DNA methyltransferase from Gram negative bacteria (*Caulobacter crescentus*) and menaquinone methyltransferase from Gram-positive bacteria (*Bacillus subtilis*) (Benkovic et al., 2005).

Cell surface proteolytic processing of anthrax protective antigen by furin or other furin-related proteases was explored by using a high-affinity inhibitor of furin, the peptide inhibitor acetyl-Arg-Glu-Lys-boroArg pinanediol (Komiyama et al., 2005). Inhibition of killing was dose dependent and correlated with prevention of protective antigen processing.

Various bacteria produce boron-containing antibiotics such as boromycins, aplasmomycins, borophycins and tartrolons.

2.1.1. Boromycins

Streptomyces antibioticus isolated from the soil of Ivory Coast contained the antibiotic boromycin (Hutter et al., 1967) (**2**) that inhibits growth of Gram-positive bacteria, but has no effect on some Gram-negative bacteria and fungi. It is also active against protozoa of the genera plasmodiae and babesiae (Prelog et al., 1973) and has been used for the treatment and prevention of coccidiosis in susceptible poultry (Miller and Burg, 1975). Boromycin was found to strongly inhibit the replication of HIV-1 (Kohno et al., 1996). It also inhibits the synthesis of protein, RNA and DNA in whole cells of *Bacillus subtilis* (Pache and Zahner, 1969). It is being antagonized by surface-active compounds and is bound to lipoprotein. Within the cell, boromycin binds to the cytoplasmic membrane. The K^+, Na^+-ATPase of the cytoplasmic membrane is not influenced by boromycin. Hydrolytic removal of boric acid from the molecule leads to a loss of antibiotic activity.

The two minor products (**3**, **4**) (*N*-formyl of **2**, *N*-acetyl of **2**) of boromycin fermentation described by Lee et al. (1985) differ in that acylation has occurred not on the 9-hydroxyl group but on the nitrogen of the valine moiety.

2.1.2. Aplasmomycins

A boron-containing antibiotic, aplasmomycin (**5**), isolated from a strain of *Streptomyces griseus* found in sea sediment in Sagami Bay, Japan (Okami et al., 1976) inhibits Gram-positive bacteria including mycobacteria *in vitro*. *S. griseus* has produced two other minor components, aplasmomycins B and C (Sato et al., 1978); an aplasmomycin C-producing actinomycete was isolated from a sandy sediment in California (Stout et al., 1991). The antibacterial activity of aplasmomycin B (**6**) was nearly equal to that of aplasmomycin (**5**), while aplasmomycin C (**7**) showed a weaker activity (Tables 2 and 3). The ability to form complexes with other metals did not directly correspond with antibacterial activity. Cation selectivity decreased in the order Rb > K > Cs = Na > Li, no affinity towards divalent cations being found.

Incubation of *S. griseus* strain SS-20 with labeled precursors ([1-^{13}C, 2-^{13}C, 1,2-^{13}C]acetates and L-[methyl-^{13}C]methionine) elucidated the biosynthetic origin of aplasmomycin (Fig. 2) (Chen et al., 1979). Surprisingly, the methyl branches in the polyketide chain come from the methyl group of methionine, in contrast to most macrolide antibiotics in which chain branches are formed by utilization of propionate units. Unusual is also the mode of incorporation of glycerol and particularly the fact that it is a

Table 2
Biological activity of aplasmomycins

Compounds	*Bacillus subtilis*[a]	*Staphylococcus aureus*
7	21.5	22.0
8	22.0	22.0
9	11.0	10.5

[a] Diameter of inhibition zone with **7**–**9** (500 μg/ml) determined by the disk diffusion method.

Table 3
Relative affinity of aplasmomycins for various cations

Cations	**7**	**8**	**9**
Na	0.27	0.40	0.45
K	1	1	1
Rb	1.1	1.4	1.5
Cs	0.9	0.6	0.8
Li	0.12	0.15	0.11
Mg	10^{-2}	$<10^{-2}$	$<10^{-2}$
Ca	10^{-2}	$<10^{-2}$	$<10^{-2}$

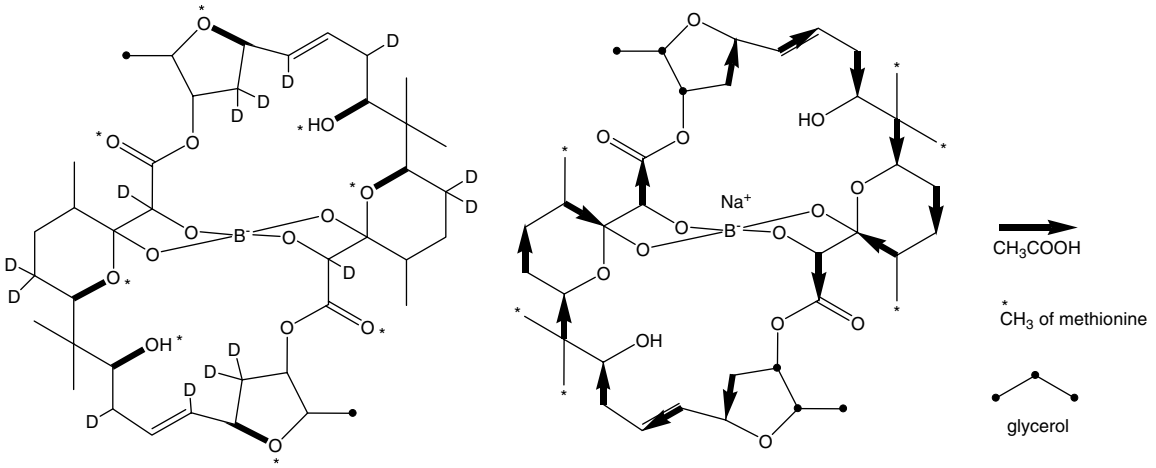

Fig. 2. Biosynthetic origin of aplasmomycin.

specific precursor of the three-carbon polyketide chain starter unit (Chen et al., 1981). Experiments with isotopically (D, T, ^{13}C and ^{18}O) labeled precursors point to phosphoglyceric acid or phosphoenolpyruvate as the glycerol-derived polyketide chain starter unit, ruling out serine, methylglyoxal, and pyruvate (Lee et al., 1987), see Fig. 2.

Aplasmomycins can be used for modifying rumen metabolism in cattle, sheep, goats, and/or deer, reducing the proportion of methane formed, and increasing the proportion of propionate (Ac/Pr) and butyrate (Ac/Bu) at the expense of methane and/or acetate (Davies and Norris, 1980); this is believed to improve growth in ruminant animals.

2.1.3. Borophycin

Borophycin (**8**) was isolated from the blue-green alga *Nostoc linckia* (Arai et al., 2004). It is made up of two identical halves with an overall structure reminiscent of other boron-containing antibiotics. The C3 starter unit for the biosynthesis of **8** is derived from acetate and methionine, but not propionate. Borophycin and four new cyclic hexapeptides containing no boron, tenuecyclamides A–D, were also isolated from the methanol extract of *Nostoc spongiaeforme* var. *tenue* collected in the Volcani Center, Israel (Banker and Carmeli, 1998).

2.1.4. Tartrolons

In a screening of myxobacteria for antibacterial metabolites, the *Sorangium cellulosum* strain So ce678 was selected for its activity against *Staphylococcus aureus* (Schummer et al., 1994, 1996; Irschik et al., 1995). The active compounds were two rather lipophilic tartrolons B (**9**) and C (**10**). Tartrolon B is a boric acid ester of tartrolon A3, whereas tartrolon A1 and tartrolon A2 are stereoisomers of tartrolon A3. All components could be chemically converted into each other. Tartrolon C (**10**) was also isolated from a *Streptomyces* species (Lewer et al., 2003). It was active on the beet army worm and tobacco bud worm, with minimum emergent larvicide concentration of 125 mg/kg on both insects, approximately 40× and 310× less active than a standard of spinosyn A.

Tartrolons acted against Gram-positive bacteria with similar MIC values. Gram-negative bacteria, yeasts, and fungi were insensitive, but mammalian cells were strongly inhibited, especially by tartrolon B. Tartrolon B inhibited the syntheses of several important cellular macromolecules in *S. aureus* but had no effect on isolated RNA polymerase and DNA polymerase from *E. coli*. Hence, tartrolon acts either specifically on enzymes of Gram-positive bacteria or, more probably, it interferes with energy delivery or membrane integrity.

Experiments with feeding the production strain *Sorangium cellulosum* with sodium [1-^{13}C]acetate, [$^{13}CH_3$]methionine, and sodium [1,2-$^{13}C_2$]acetate were performed to investigate the biosynthesis of the tartrolons (Schummer et al., 1996), see Fig. 3.

The result is in good agreement with boromycin and aplasmomycin where C-1 to C-14 are derived from seven acetate units, and with borophycin (see above) where C-1

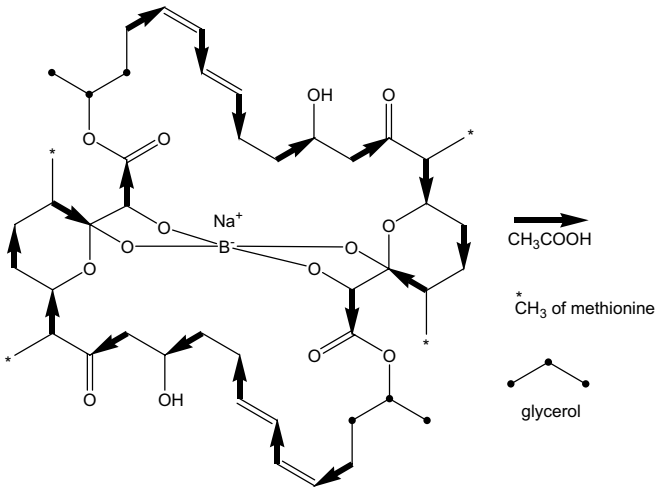

Fig. 3. Biosynthesis of tartrolon.

to C-16 are derived from eight acetate units. Whereas the three-carbon starter unit, C-15 to C-17 in boromycin and aplasmomycin, is derived from glycerol, C-17 to C-19 in borophycin are derived from acetate and methionine. Thus, regarding the biosynthesis, tartrolon is closely related to boromycin and aplasmomycin, whereas borophycin with a propionyl starter unit derived from acetate and methionine exhibits a more distant relation.

2.2. Boron in plants

Boron–polysaccharide complexes were isolated from cell walls of tomato leaves and later from radish (*Raphanus sativus*) roots (Yamauchi et al., 1986; Matoh et al., 1993). One of the complexes, the 7.5 kDa BR-II, contained boron (23%), uronic acid (52%) and neutral sugars (32%). ^{11}B NMR analysis showed boron to be present as a tetravalent 1:2 borate–diol complex (Ishii and Matsunaga, 1996). BR-II links with two rhamnogalacturonan-II chains, which include apiose, aceric acid (3-*C*-carboxy-5-deoxy-L-xylose), 2-*O*-methyl-fructose, 3-deoxy-D-manno-2-octulosonic acid (Kdo), rhamnose, galactose, arabinose, 2-*O*-methyl-L-fucose, fucose, 2-*O*-methyl-D-xylose, galactouronic acid, and glucouronic acids residues (Ishii and Matsunaga, 1996). Partially acid hydrolyzed BR-II complex from sugar beet (*Beta vulgaris*) was found to consist of two disaccharide moieties: α-L-Rhap-(1 → 5)-D-Kdo and α-L-Araf-(1 → 5)-Dha (3-deoxy-D-*lyxo*-heptulosaric acid), an aceric acid-containing oligosaccharide (Ishii and Kaneko, 1998). The monosaccharide constituents of BR-II complexes are interconnected by at least 100 different glycosidic linkages (Ishii and Matsunaga, 2001). Chemical fragmentation of the BR-II isolated from the walls of suspension-cultured sycamore (*Acer pseudoplatanus*) cells led to the isolation and structural characterization of two 3-deoxysugar containing disaccharides, i.e., α-L-Rhap-(1 → 5)-D-Kdo (York et al., 1985) and β-L-Araf-(1 → 5)-D-Dhap (Stevenson et al., 1988). Other boron-containing complexes include, e.g., two structures of furanoidic cis-1,2-diol borate esters: 1,4-anhydroerythritol (**11**) and methyl β-D-ribofuranoside (**12**) (Benner and Klufers, 2000).

Boron is an essential nutrient for plants but is toxic at high levels (Takano et al., 2005). Many plants are known to reduce the toxic effects of high soil boron (B) by reducing uptake of B, but no mechanism for limiting uptake has previously been identified (Hayes and Reid, 2004). Uptake studies (Dannel et al., 2002) indicated that xylem loading is the key step for boron accumulation in shoots with a low external boron supply (Takano et al., 2002).

The model plant *Arabidopsis thaliana* was used to examine the mechanisms protecting plants from B deficiency. In it, Takano et al. (2002) identified BOR1, a membrane protein with homology to bicarbonate transporters in animals as an efflux-type B transporter for xylem loading that is essential for protecting shoots from boron deficiency. A potential BOR1 homolog was found also in Eucalyptus (Domingues et al., 2005).

Miwa et al. (2006) generated *Arabidopsis thaliana* plants tolerating B-deficient conditions due to the overexpression of BOR1. Transgenic plants expressing BOR1 or BOR1-GFP under the control of the cauliflower mosaic virus 35S RNA promoter showed enhanced root-to-shoot translocation of B and greater shoot growth under B-limiting conditions than wild-type plants. In contrast to wild-type plants, they set seed normally under B-limiting conditions. BOR1 accumulation in cells is regulated by posttranscriptional mechanisms (Takano et al., 2005). Under B limitation BOR1 is localized to the plasma membrane. Upon B supply it is transferred from the plasma membrane via the endosomes to the vacuole for degradation. Hence endocytosis and degradation of BOR1 are regulated by B availability, to avoid accumulation of toxic levels of B in shoots under high-B supply, while protecting the shoot from B deficiency under B limitation.

Transcriptome analysis of *Arabidopsis thaliana* under conditions of both low and high B identified nine genes induced by high B in roots and shoots (Kasajima and Fujiwara, 2007). They included genes coding for transcription factors, multidrug and toxic compound extrusion transporters and heat shock proteins.

In *Arabidopsis thaliana*, Takano et al. (2006) identified NIP5;1, a member of the major intrinsic protein family, which is strongly upregulated in the root elongation zone and the root hair zone under B limitation and is localized in the plasma membrane, as a major plasma membrane boric acid channel crucial for the B uptake required for plant growth and development under B limitation.

A borate anion efflux transporter extruding actively B from the root was proposed to be responsible for low B concentrations in the roots, xylem and leaves in a B-tolerant cultivar of barley (Hayes and Reid, 2004).

In tobacco, boron deficiency was found to decrease net nitrate uptake by reducing the activity of nitrate transporters (Camacho-Cristóbal and González-Fontes, 2007). This could lead to an activity decrease in the plasma membrane H^+-ATPase exporting from the cells protons needed for inward cotransport with nitrate. Boron deficiency may also promote ammonium assimilation via asparagine synthetase in tobacco roots.

2.3. Boron in aquatic organisms

The water-soluble cell wall sulphated polysaccharide ulvan from the green seaweed *Ulva* sp. contains (1 → 4)-β-D-GlcpA-(1 → 4)-α-L-Rhap 3-sulphate and (1 → 4)-α-L-IdopA-(1 → 4)-α-L-Rhap 3-sulphate named ulvanobiuronic acid 3-sulphate A and B, respectively. The ring hydroxyl groups of these repeating structures contain the iduronic acid rarely encountered in plant polysaccharides (Lahaye et al., 1998). Free and complex forms of borate in marine green (*Ulva fasciata* and *U. pertusa*), brown (*Laminaria japonica* and *Undaria pinnatifida*), and red algae (*Gloiopeltis tenax* and *Grateloupia turuturu*) were identified by ^{11}B NMR (Chuda et al., 1997). Boron also forms complexes

with compounds containing vicinal hydroxy groups, such as mannitol, laminarin, and alginic acid (Chuda et al., 1997).

2.4. Boron in animals

Whereas the role of boron in the life cycle of plants is well documented, very little is known about boron homeostasis and function in animal cells (Park et al., 2004) although it is also beneficial or has been established as essential for several animal models of human nutrition (Ralston and Hunt, 2004). Experiments with Abelson leukemia virus BALB murine monocyte-macrophage RAW 264.7 and HL60 cells indicated the existence of a selective boron-binding molecular species within the cell or the existence of a boron-specific membrane transporter in mammalian cells (Ralston and Hunt, 2004).

The boron transporter NaBC1, the mammalian homolog of AtBor1, functions as a borate transporter essential for cell growth and proliferation (Park et al., 2004, 2005). In the absence of borate, NaBC1 conducts Na^+ and OH^- (H^+), while in the presence of borate it functions as an electrogenic, voltage-regulated, Na^+-coupled $B(OH)_4^-$ transporter. At low concentrations, borate activates the MAPK pathway to stimulate cell growth and proliferation, while at high concentrations it is toxic.

2.5. Conclusion

Boron is an essential trace element for plants and is beneficial for animals and humans. Dietary boron obviously plays a role in immune functions. Among the best-known natural boron-containing compounds are polyketide antibiotics such as boromycin, aplasmomycins, borophycin, and tartrolons. Attempts are underway to incorporate boron into different biologically active molecules, particularly for medicinal application, e.g. for boron neutron capture therapy of brain tumors. Some boron-containing biomolecules may apparently act as signaling molecules that interact with cell surfaces.

3. Silicon

Silicon, tetravalent metalloid, is less reactive than its chemical analogue carbon. It is the second most abundant element in the Earth's crust, making up 25.7% of it by weight. Elemental silicon is not found in nature. It occurs mainly in the form of silicon dioxide – silica – and silicates that contain silicon, oxygen, and metals. Amethyst, agate, quartz, rock crystal, flint, jasper, and opal are some of the forms in which the oxide appears. Granite, asbestos, feldspar, clay, hornblende, and mica are a few of the many silicate minerals. Its concentration in seawater is relatively low, only 3 mg/L (Tacke and Becker, 1987).

Chemically, silicon is similar to carbon but differs from it in many features. Silicon atoms are much bigger and they have difficulty forming double or triple bonds. Alkane analogues silanes are highly reactive with water, and long-chain silanes spontaneously decompose. Molecules incorporating Si–O–Si bonds instead of Si–Si bonds are much more stable; ordinary sand is one such example (Tacke and Wagner, 1998).

Silicon is a biogenic element, although its content in the tissues of living organisms is not very high. In contrast to carbon, silicon has a powerful affinity for oxygen. In respiratory processes of terrestrial organisms, carbon is oxidized to carbon dioxide that is easy to remove from the body. The oxidation of silicon, however, yields a solid silicon dioxide that forms a lattice in which each silicon atom is surrounded by four oxygens. Disposing of such a substance would pose a major respiratory challenge.

In carbon life forms, the basic energy storage compounds are carbohydrates and lipids in which the carbon atoms are linked in most cases by single bonds into a chain. Their oxidation in a series of controlled steps yields energy and the waste products water and carbon dioxide. Importantly, many carbon compounds can take right and left forms; this handedness, or chirality, gives enzymes their ability to recognize and regulate a huge variety of processes in the body. Silicon does not give rise to many compounds that display handedness and could thus hardly serve as the basis for the many interconnected chains of reactions needed to support life (Muller, 2003).

In addition to the formation of silicon compounds in nature, the bioorganic chemistry of silicon focuses on synthetic organosilicon compounds. These compounds, though not of natural origin, deserve our attention since they can shed light on some of the mechanisms and interactions taking place in nature (Mills and Showell, 2004; Tacke, 1999).

3.1. Silicon in bacteria

Silicate bacteria, members or relatives of the genus *Bacillus*, release silicon from aluminosilicates through the secretion of organic acids (Groudev, 1999). Microbes and microbial enzymes have been used in the biotransformation of organosilicon compounds and biodegradation of organosilicon under aerobic (Sabourin et al., 1996) and anaerobic (Grumping et al., 1999) conditions has been described.

3.2. Silicon in fungi and plants

Some organic acid producing fungi (*Aspergillus niger*, *Serpula himantioides* and *Trametes versicolor*) were tested for causing fungal weathering of apatite, galena, and obsidian. Physico-chemical interactions of fungal metabolites, e.g. H^+ and organic acids, with the minerals appear to be the primary driving forces of the process (Adeyemi and Gadd, 2005). The fungi were capable of mineral surface colonization, corrosion of the mineral surface and secondary mineral formation. The (micro)biological and

rhizosphere processes contributing to Si mobilization, plant uptake, and formation of phytogenic Si in plants, and release due to microbial decomposition were reviewed by Sommer et al. (2006). Si transporters in some plants, e.g. rice, have been described (cf. Ma et al., 2006; Ma and Yamaji, 2006).

In plant cells, increased silicon content can be found, e.g., in horsetail or shave grass, and in stimuli of stinging nettles. Intra-silica proteinaceous materials have been extracted from *Equisetum telmateia* (great horsetail) and *E. arvense* (common horsetail), and from hairs found on the lemma of the grass *Phalaris canariensis*. They contain protein and carbohydrate components enriched in xylose and glucose. The amino acid compositions of the matrices contain around 25 mol% serine/threonine and 20 mol% glycine (Bains and Tacke, 2003).

Silicon is effective in controlling various plant pests and diseases caused by both fungi and bacteria, and alleviating various abiotic stresses including salt stress, metal toxicity, drought stress, radiation damage, nutrient imbalance, high temperature, freezing, etc., preventing lodging (falling over) and increasing resistance to other stresses and enhancing the quality and yield of agricultural crops (Ma, 2004, 2005), since it can apparently modulate the timing and extent of plant defense responses in a manner reminiscent of the role of secondary messengers in induced systemic resistance. It can also bind to hydroxyl groups of proteins involved in signal transduction, or can interfere with cationic co-factors of enzymes influencing pathogenesis-related events. It may therefore interact with several key components of plant stress signaling systems leading to induced resistance (Fauteux et al., 2005). The beneficial effects of Si are usually expressed more clearly in Si-accumulating plants and are mainly attributed to the high accumulation of silica on the tissue surface although other mechanisms have also been proposed. Plants greatly vary in their ability to take up Si from the soil and load it into the xylem. Genetically manipulating the Si uptake capacity of the root might help some plants to accumulate more Si and, hence, improve their ability to overcome biotic and abiotic stresses. The use of rice mutants that are deficient in silicon uptake, application of electron-energy-loss spectroscopy and the knowledge of the complete sequence of the genomes for a dicotyledonous (*Arabidopsis*) and a monocotyledonous (rice) available for large-scale genetic analysis will help to elucidate the role of silicon in heavy metal tolerance (Richmond and Sussman, 2003).

Rice, a typical silicon-accumulating plant, accumulates up to 10% silicon in the shoot, and this high accumulation is required to protect the plant from multiple abiotic and biotic stresses. Silicon deposition in exodermis and endodermis of rice root reduces sodium transport through the apoplastic pathway, which is tightly associated with salt tolerance (Gao et al., 2007). Ma et al. (2006) described a low silicon rice 1 (Lsi1) gene, which controls silicon accumulation, belongs to the aquaporin family and is constitutively expressed in the roots. Lsi1 is localized on the plasma membrane of the distal side of both exodermis and endodermis cells in the basal zone of roots (Yamaji and Jian, 2007). Subsequently, Ma et al. (2007) described an Lsi2 gene, which has no similarity to Lsi1 and is also constitutively expressed in rice roots. Like Lsi1, the protein encoded by this gene is localized on the plasma membrane of exodermis and endodermis cells. In contrast to Lsi1, which is localized on the distal side, Lsi2 is localized on his proximal side of the same cells. Having an influx transporter on one side and an efflux transporter on the other side of the cell permits the plants to carry out an effective transcellular transport of nutrients.

3.3. Silicon in aquatic organisms

Silicon is an important building block of unicellular algae – diatoms. The main building material of the frustule (the finely sculptured protective surface layer of diatoms) is a float-stone, an opal-like water-containing polymer of silica. Diatoms are the only group of organisms whose development is totally dependent on the presence of soluble forms of silica in the environment. When silicon sources run out, DNA replication stops. Diatom silicon transporters (SITs), which generally group according to species, were the first proteins shown to directly interact with silicon. Full-length SIT genes were identified from the pennate diatom *Nitzschia alba* (Lewin and Lewin), and the centric diatom *Skeletonema costatum* (Greville) Cleve. There are structural differences between SITs of centrics and pennates, suggesting differences in transport mechanism or regulation (Thamatrakoln et al., 2006).

Organic molecules have a crucial role in the formation of biosilica owing to the specificity of interactions at the organic–inorganic interface (Foo et al., 2004; Perry and Keeling-Tucker, 2000; Brandstadt, 2005; Englebienne et al., 2005). Biosilicification has been studied most extensively in diatoms. As mentioned above, dissolved silicon in seawater occurs mostly as the undissociated orthosilicic acid, $Si(OH)_4$. Many marine organisms, such as diatoms, silicoflagellates, radiolarians, and sponges, contain silica skeletons ($SiO_2 \times nH_2O$) that are built up by taking up orthosilicic acid from seawater. The diatom cell wall (frustule) is made of nanostructured amorphous silica that is associated with polysaccharides and proteins. New cell walls are produced in a silica deposition vesicle (SDV); soluble silicon is taken up from the environment and concentrated in SDV, and here the insoluble silica is formed and subsequently secreted. As the environmental concentrations of dissolved silicon are rather low, diatoms must have an efficient transport system forming an integral part of the silicification process. Orthosilicic acid is transported into the cell and then intracellularly into the SDV where silica formation occurs. A protein that transports silicon from seawater into the cell of the diatom *Cylindrotheca fusiformis* has been characterized; however, silicon transporter proteins of this particular type are not necessarily involved in intracellular transport.

Some data correlate distinct silica elements with specific proteins within the diatom cell wall. The cell wall of *C. fusiformis* contains frustulins, pleuralins, and silaffins. Frustulins, extracted from the cell wall with EDTA, consist of four (α, β, γ, δ) Ca^{2+} binding glycoproteins with molecular weights ranging from 75 to 200 kDa. The major component, 1-frustulin, is one of a number of isoforms of a 75 kDa protein that is immunologically related to proteins extracted from the cell walls of other diatom species, namely *Navicula pelliculosa*, *Nitzschia alba*, *N. angularis* and *Phaeodactylum tricornutum*. Each frustulin contains at least three of five structural elements: (1) presequence domain, (2) acidic cysteine-rich domain with a highly repetitive structure, its common sequence being C-E/Q-G-D-C-D, (3) proline-rich domains, (4) polyglycine domains, and (5) a tryptophan-rich domain (Kroger et al., 1997).

Three HF-extractable proteins, pleuralin 1 (200 kDa), pleuralin 2 (180 kDa), and pleuralin 3 (150 kDa) are involved in the formation of new theca (one of the halves in the cell wall) when one parental diatom is divided into two daughter diatoms (Kroger and Wetherbee, 2000).

The silaffins induce and regulate silica precipitation at ambient temperature and pressure. Native silaffins (natSil) including natSil-1A (6.5 kDa), natSil-1B (10 kDa), and natSil-2 (40 kDa), were detected by treating the diatom cell wall with NH_4F. They are highly post-translationally modified and some functional groups such as phosphate, sulfate, and carbohydrate are lost during the process of dissolving the cell wall with HF, resulting in lower molecular weight proteins: silaffin-1A (4 kDa), silaffin-1B (8 kDa), and silaffin-2 (17 kDa) proteins. A gene *sil 1* has been isolated from a *C. fusiformis* genomic library that encodes a polypeptide of 265 amino acids. Seven repeat sequences were identified in *sil 1* and termed R1 to R7. R1 and R2 peptides correspond to the precursors of silaffin-1B and silaffin-1A2, respectively, whereas R3–R7 peptides correspond to the precursors of silaffin-1A1 (Poulen et al., 2003).

As shown by Fachini and Vasconcelos (2006), synthetic products of zeolitic nature significantly promoted the growth of the diatom *Phaeodactylum tricornutum* by acting as a silicon buffer while providing a source of silicon required for growth, and releasing into the seawater small amounts of the limiting micronutrient manganese and removing zinc from it.

3.4. Conclusions

Silicon is essential for growth and biological function in a variety of plant and microbial systems but the molecular mechanisms of these interactions are still unknown. Studies testing the ability of homologous enzymes to catalyze the formation and cleavage of siloxane bonds enable us to better understand the role of various proteins in the biosilification process. Genetic engineering and biotechnological methods are used to develop new, environmentally benign routes to the synthesis of organyl-substituted siloxanes. It can be expected that further studies of the proteins, genes, and molecular mechanisms controlling silicon metabolism in diatoms may help to reveal the mechanisms involved in the essential requirement for silicon for optimal development and growth in many plants.

4. Arsenic

Arsenic, the twentieth most abundant element in the Earth's crust, is widely distributed in the environment, mainly associated with sulfide minerals. Its content in soils is 0.5–35 mg/kg (Yan-Chu, 1994; Walsh and Keeney, 1975; Leonard, 1991). The most important anthropogenic arsenic sources are the smelting of Cu, Ni, Pb, and Zn ores and the burning of fossil fuels in households and power plants. Coal burning causes the emission of arsenic by volatilization of As_4O_6, which condenses in the flue system (Bhumbla and Keefer, 1994). Another anthropogenic source of arsenic contamination was the use of arsenical fungicides, herbicides, and insecticides in agriculture and wood industry. Organically bound arsenic (diphenylchloroarsine (**13**), diphenylcyanoarsine (**14**), phenyldichloroarsine (**15**)) was used as warfare and dimethylarsinic acid (**16**) (agent blue, cacodylic acid) was used during the Vietnam War for defoliation for military purposes (Gorby, 1994). Until the discovery of antibiotics, arsenic compounds were widely used in medicine for the treatment of a variety of illnesses.

Arsenic is considered to be an essential element but many arsenic compounds are toxic (Mayer, 1993). Organic arsenic compounds are less toxic than inorganic ones.

Acid-rock drainage results from the exposure of sulfide minerals, particularly pyritic and pyrrhotitic minerals, to atmospheric oxygen and water. The primary removal is caused by sulphate-reducing bacteria (SRB), obligate anaerobes growing at pH 5–8 that facilitate the conversion of sulphate to sulphide. Other oxyanions such as arsenate can be removed using the wetland treatment system (passive bioreactor) technology, which is less expensive than the conventional chemical precipitation. Arsenic is removed as an arsenic sulfide compound (Cohen, 2006).The sulphides react with metals to precipitate them as metal sulfides, many of which are stable in the anaerobic conditions of the treatment systems.

As(III) and As(V) in organic (phenylarsine oxide, phenylarsonic acid, dimethylarsinic acid, monomethylarsonic acid) and inorganic form (arsenite, arsenate) were incubated with sulfur-containing amino acid, peptide and protein solutions. Incubation of phenylarsine oxide with cysteine and glutathione gave rise to a covalent bond between arsenic and sulfur stable at both acidic and neutral pH values; mass spectra were dominated by monovalent ions at m/z 272 for cysteine and at m/z 458 for glutathione, indicative of covalent arsenic–sulfur complexes or other arsenic-bonding sites presumably at the amino group. No interactions of inorganic arsenite or arsenate could be measured under the same conditions. No interactions with

arsenic could be detected for the model protein lysozyme, whereas thioredoxin showed As bonding that depended on the concentration of a disulfide-reducing agent.

The mass spectra of three different phenylarsonic acids and of dimethylarsinic acid containing pentavalent arsenic displayed the presence of complexes with glutathione that can be due to non-covalent interactions or to a covalent bond caused by an additive reaction (Schmidt et al., 2007).

4.1. Arsenic in fungi

Levels of total arsenic and arsenic compounds were determined in terrestrial fungi, *Paxillus* sp., *Psathyrella* sp., *Leccinum* sp., *Coprinus* sp., *Lycoperdon* sp. (Giant Mine), and *Lycoperdon* sp. (Con Mine), from Yellowknife (Slejkovec et al., 1997). 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 arsenobetaine (**17**). Arsenobetaine (**17**) was also observed to be the major arsenic species extracted from *L. echinatum* (78%), *L. perlatum* (88%), and *L. pyriforme* (62%); minor components included As(III), As(V), **16**, and **18** (Larsen et al., 1993). The arsenobetaine (88% of extracted arsenic) was determined as the water-soluble species in the mushroom *Coprinus comatus*. Minor components included arsenocholine (**19**), **20** and an unknown arsenic compound (Larsen et al., 1993). Arsenic content of *Paxillus involutus* was unusual because a major proportion of extracted arsenic (36%) was in an unidentified form (Kuehnelt et al., 1997).

The main arsenic compound found in many mushrooms (Agaricales and Aphyllophorales) was **17**. Dimethylarsinic and methylarsonic acids were present in many mushrooms, but generally as minor components. *Collybia butyracea* contained mainly **17** (8.8 mg/kg) and dimethylarsinic acid (**16**) (1.9 mg/kg). In *Laccaria laccata*, *Leucocoprinus badhamii*, and *Volvariella volvacea*, **16** was the major metabolite. Arsenocholine (**19**) and the tetramethylarsonium ion (**21**) were present in a few species, generally in low concentrations. Arsenobetaine (**17**) was the main compound in *Sparassis crispa* (Bender et al., 1995). Kartal et al. (2006) studied the potential of mold and staining fungi, *Aspergillus niger*, *Aureobasidium pullulans*, *Gliocladium virens*, *Penicillium funiculosum*, *Rhizopus javanicus*, *Ceratocystis pilifera*, *C. peceae*, *Alternaria alternata*, *Trichoderma viride*, and *Cladosporium herbarum*, to remove copper, chromium, and arsenic elements from chromated copper arsenate treated wood. Arsenic removal (30–90%) was species-dependent. The data show that fungal remediation processes can remove inorganic metal compounds via organic acid production, increasing the acidity of the substrate and increasing the solubility of the metals.

4.2. Arsenic in plants

Arsenic(III), arsenic(V), **16**, and **18** have also been found in many vegetables and fruits: garlic, onion, potato, carrot, beetroot, spinach, asparagus, cabbage, rice, radish, chard, corn, tomato, and beans, their concentrations varying depending on the locations (Munoz et al., 2002; Abedin et al., 2002; Watanabe et al., 1979). The plants that take up and accumulate more than 1000 μmol As/g dry weight were named hyperaccumulators (Brooks et al., 1977). A report about an arsenic-hyperaccumulating fern species discussed the phytoremediation potentials of such plants (Koch et al., 2000). Recent investigation has shown that the arsenic compounds in terrestrial and aquatic plants, fungi, and lichen species are also interesting natural products (Edmonds et al., 1993; Eisler, 2000).

The extracts of the plants *Trifolium pratense*, *Dactylis glomerata*, and *Plantago lanceolata* contain inorganic arsenic such as As(III), As(V), besides the simple methylated compounds **16**–**19**, and **21**–**22**. The main organoarsenic detected in *Dactylis glomerata* and *Plantago lanceolata* was **20**. Small amounts of **17**, **21**, **22** were present in all three species, whereas **19** was only detected in *Plantago lanceolata*.

Organoarsenic compounds found in green plants, namely *Achillea millefolium*, *Alnus incana*, *Asplenium viride*, *Dryopteris dilata*, *Deschampsia cespitosa*, *Equisetum pratense*, *Fragaria versa*, *Larix decidua*, *Picea abies*, *Rubus idaeus*, *Vacciniun myrtilis*, and *Vaccinium vitis idaea* as well as two lichen species, *Alectoria ochroleuca* and *Usnea articulata* (Kuehnelt et al., 2000) were found to include **16**–**19**, and **23**. The maximum was determined in the lichen *A. ochroleuca*, i.e. 77 μg/kg dry weight. Acid **18** was found in *Agrostis scabra* (0.6%) and *Hordeum jubatum* (3.6%) from Yellowknife, Northwest Territories in Canada (Kuehnelt et al., 2000). Terrestrial grasses, *Bidens cernua*, *Carex* sp., *Equisedum fluviatile* and *Typha latifolia*, as well as terrestrial plants, contain also compound **18**. Arsenous acid, arsenic acid, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, trimethylarsine oxide and glycerol-ribose were detected in two lichen species from an arsenic-contaminated environment: epiphytic *Hypogymnia physodes* (L.) Nyl. and terricolous *Cladonia rei* Schaer. In addition, *H. physodes* contained phosphate-ribose (Mrak et al., 2006).

The influence of soil contamination by inorganic and organic arsenic compounds on uptake, accumulation, and transformation of arsenic was investigated in tomato (*Lycopersicon esculentum*) and pepper (*Capsicum annum* L.) plants cultivated in the presence of arsenite, arsenate, methylarsonic acid (MA), and dimethylarsinic acid (DMA) (Tlustos et al., 2006; Szakova et al., 2007). In both species, the plant availability of the arsenicals increased in the order arsenite = arsenate < MA < DMA. The arsenic contents in tomato plants decreased during vegetation period. Arsenic level in tomato plants decreased in the order roots > leaves > stems > fruits, in pepper plants the order was roots > stems > leaves > fruits regardless of arsenic compound applied. In tomato plants, arsenic toxicity was the strongest with DMA.

Knowledge of arsenic speciation in plant tissues is important for understanding how terrestrial plants take up, trans-

port and metabolize different arsenic species. Arsenic species can be transformed from one form to another during sample preparation and the measurement process. Quaghebeur and Rengel (2005) described the methods used to measure arsenic speciation in plant tissues. Arsenic phytotoxicity stems from changes in the permeability of the cell membrane, reactions with –SH groups, reactions with phosphate groups and active groups of ADP or ATP and replacement of essential ions (Patra et al., 2004). It depends on As concentration and chemical form in the soil. Due to its similarity to phosphorus, As participates in many cell reactions and has been reported, e.g., to replace P in the phosphate groups of DNA. Arsenites and arsenates may interfere with biochemical processes in plants that involve SH groups and phosphorus. As can act as an effective mitotic poison and induce various types of spindle disturbances. The clastogenic effects are S-dependent, are affected by the availability of cations and are related directly to the dosage and duration of exposure. As(III) is a weak mutagen but potent comutagen. Metal tolerance in plants can include metal sequestration by specially produced organic compounds, compartmentation in certain cell compartments, metal ion efflux and organic ligand exudation. Inside cells, proteins such as ferritins and metallothioneins, and phytochelatins participate in excess metal storage and detoxification. When these systems are overloaded, oxidative stress defence mechanisms are activated.

4.3. Arsenic in aquatic organisms

Arsenosugars such as glycerol-ribose **23** and phosphate-ribose **24** as well as acid **18** were found in aquatic plants (submergents) such as *Lemna minor*, *Myriophyllum* sp., and *Sparganium augustifolium*.

The marine brown alga *Hizikia fusiforme* (phylum Sargassaceae) contained acids **16** and **18** in addition to inorganic arsenic and other unknown organic compounds (Edmonds and Francesconi, 1987; Edmonds et al., 1987; Maitani et al., 1987). Algae of the *Hizikia* species contain also arsenosugars such as **23**–**27**. *Laminaria japonica* (Francesconi, 2002) and *Laminaria digitata* (McSheehy et al., 2000) contained **16**–**19**, and **23**–**26**, as well as novel organo-arsenic compounds **27**–**29**.

Arsenic-containing ribofuranosides **23**–**26** have been isolated from *Laminaria* sp. (Edmonds, 2000). Compound **30** and two diastereoisomers **31** and **32** were found as major compounds (Edmonds and Francesconi, 1983). Compounds **23**–**26** as well as inorganic arsenicals have been isolated from the Australian brown kelp *Ecklonia radiana* (Tukai et al., 2002).

A study of the level 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*, and *Ulva lactuca* collected from the coastline near Sydney (Geiszinger et al., 2001) revealed the presence of three major arsenoribosides **24**–**26** in all species. Biotransformation of arsenic by the brown alga *Fucus serratus* showed the presence of arsenite, arsenate, **16**, **18**, and arsenosugars **23**–**26** (Wrench et al., 1979).

Some studies of the arsenic compounds in algae (Irgolic et al., 1977) involved the growth of microalgae, *Tetraselmis chuii* (Cooney et al., 1978) and *Chaetoceros concavicornis* (Kaise et al., 1999) in media containing radiolabeled arsenate.

Unicellular microalgae, *Chladomydomonas reihardtii* (Cullen et al., 1994) and *Polyphysa peniculus* (Kuroiwa et al., 1994) as well as green algae *Chlorella* sp. (Kaise et al., 1997), *Chlorella vulgaris* (Maeda, 1994), and *Phormidium* sp. (Yamaoka et al., 1999) can accumulate and biotransform inorganic arsenic to methylated species. Other marine microalgae, such as *Dunaliella salina*, *Chattonella antiqua*, *Heterosigma akashimo*, *Skeletonema costatum*, *Chaetoceros debile*, and *Thalassiosira weissflogii* (Li et al., 2003), are tolerant to arsenate and accumulate As(III) and As(V) in high concentrations, and can transform arsenic(III) and arsenic(V) acids to other arsenic species such as **16**, **18**, and **20**.

The total arsenic concentrations of *Porphyra* collected from the China Sea ranged from 2.1 to 21.6 mg/kg (Wei et al., 2003). Arsenosugars were the only arsenic species that could be detected in all samples. Arsenosugar PO_4 (**24**) was the major compound in most samples (up to 13.9 mg/kg of dry weight), followed by arsenosugar OH (**23**) (up to 6.2 mg/kg of dry weight). The arsenosugars were stable during a short-term heating at 100 °C. The substantial increase of dimethylarsinic acid (**16**) detected in urine samples collected from six people indicated that arsenosugars had been metabolized to **16**, which is more toxic than arsenosugars.

Arsenic binding to *Fucus vesiculosus* metallothionein (a low-molecular weight metalloprotein with high cysteine content, which binds a range of metals) has been described by Merrifield et al. (2004). Five arsenic metallothioneins were detected with increasing As to protein ratios, providing important information about the metal-chelation behavior of this novel algal metallothionein, which is a putative model for arsenic binding to *F. vesiculosus in vivo*.

A study (Almela et al., 2005) examined arsenic compounds in raw and cooked edible seaweed and the bioaccessibility of arsenosugars (**23**–**26**). An *in vitro* digestion (pepsin, pH 2; pancreatin-bile extract, pH 7) was used to estimate arsenosugar bioaccessibility. Cooking of *Undaria pinnatifida* and *Porphyra* sp. did not alter the arsenic species present in the methanol–water extract, but it produced a substantial increase (2 and 5 times) in the As(V) extracted from *Hizikia fusiforme*. In all of the seaweeds analyzed, arsenosugar bioaccessibility was high (>80%) and did not vary as a result of cooking. Arsenosugar degradation as a result of *in vitro* digestion was not observed.

The concentrations of the three arsenicals (**33**–**35**) were determined in 37 marine organisms comprising algae,

crustaceans, bivalves, fish and mammals by high-performance liquid chromatography/inductively coupled plasma mass spectrometry (HPLC/ICP-MS) (Sloth et al., 2005). All three organoarsenics, which occurred at μg/kg concentrations, were detected in 25, 23 and 17 of the 37 samples analyzed, respectively. The limits of detection were 2–3 μg/kg dry mass. The data illustrate that all three compounds are common minor constituents in practically all marine samples.

The first adamantine-type polyarsenic compound ever found in nature, arsenicin A, it was isolated from the organic extract of the poecilosclerid sponge *Echinochalina bargibanti* collected from the northeastern coast of New Caledonia by Mancini et al. (2006). Arsenicin A is a bactericide and fungicide effective against human pathogens.

Lipid-soluble arsenicals (arsenolipids) may play a key role in the biosynthesis of organoarsenic compounds from inorganic arsenic. Schmeisser et al. (2005) studied arsenolipids in 10 crude fish oils from various regions of the world by using ICPMS following acid digestion with microwave-assisted heating. All fish oils contained the same 4–6 major arsenolipids in amounts depending on the origin of the fish, plus many more minor arsenolipids.

Different types of popular Chinese edible seafood, including brown algae, red algae, fish, crab, shrimp, mussels, oysters, and clams were examined for their total content of arsenic and its different compounds (Yamaoka et al., 2001). Arsenolipids such as **23**–**26** were detected in all of the extracted algae (1.5–33.8 μg/g dry weight). A major share of arsenic components in seafood was organic arsenic with a low toxicity (Yamaoka et al., 2001).

4.4. Conclusion

Arsenic is ubiquitous and arsenic compounds are present in a wide variety of environment components including terrestrial and aquatic living organisms. Arsenic can be found as part of arsenolipids, arsenosugars and many other types of compounds. Despite their known toxicity, arsenic compounds, especially organic ones, are integral components of the food chains of many organisms including humans and may play potentially important biological roles in these organisms. Their deeper and more detailed knowledge may contribute to their resurrection as medically or environmentally useful or beneficial agents.

5. Selenium

The relative proportion of selenium in the environment is very low. In the Earth's crust, selenium is present in a concentration of 0.05–0.09 mg/kg. Its level in sea water is usually 0.45 μg/kg, in stream water 0.2 μg/kg. In compounds, selenium is present as Se^{2-}, Se^{2+}, Se^{4+}, and Se^{6+}. In general, it is present in the environment in elemental form or in the form of selenide (Se^{2-}), selenate SeO_4^{2-}, or selenite SeO_3^{2-}. In soils, the identity and amounts of the various oxidation state species depend strongly on the redox-potential conditions, with the lower oxidation states predominating in anaerobic conditions and acidic soils, while the higher oxidation states are favored in alkaline and aerobic conditions. The elemental form of selenium, selenium dioxide, and volatile organoselenium compounds produced by industries and plants are incorporated in the environment. Trace amounts of selenium present in water usually as selenate or selenite are a result of geochemical processes, e.g. rock weathering and soil erosion. Se has strong affinity to coal matter – organic and (or) inorganic but is certainly authigenic. Both organic (Se-org) and inorganic selenium (Se-min) can exist in coal. In addition, Se can occur not only as a chemical-bound form, but also in sorbed (acid leachable) selenate form in the oxidized coals. There are two types of the Se-accumulations in coal: ''reducing'' and ''oxidizing''. In the first type, Se is enriched in high-sulfur coals, concentrating in sulfide phases. In coals of the second type, which are located in the areas with arid climate and enhanced Se content in water, Se is enriched in the bed oxidation zones (Yudovich and Ketris, 2006).

Although most selenium compounds are markedly toxic, considerable attention has lately been devoted to the effects of selenium shortage in the daily food intake (Table 4).

5.1. Selenium in microbial cells

Microbial dissimilatory reduction of selenate to selenite and then to elemental selenium has been described (Stolz and Oremland, 1999). Selenide undergoes biomethylation to produce methylselenide and dimethylselenide (Frankenberger and Arshad, 2001). Practically all small organic selenium compounds in plants, yeast or bacteria are the isologues of corresponding sulfur compounds, mostly sulfur amino acids or their derivatives (Tables 5 and 6).

In most cases, neither the initial steps of selenium assimilation nor the enzymes of the trans-sulfuration pathway discriminate between sulfur and selenium (Birringer et al., 2002). Usually the Michaelis constants (K_m) of these

Table 4
Examples of plants that are Se accumulators or hyperaccumulators and are used as food

Plant	Concentration (mg/kg)	Compound
Accumulators		
Wheat	0.1–15	**42**
Brazil nuts	2.0–35 and more	**42**
Mushrooms	0.1–20	Unknown[a]
Brussels sprouts	0.03–7.0	Unknown
Hyperaccumulators		
Garlic	>1200	**37**
	<300	**38**
Broccoli	~1000	**37**
Ramp	>500	**42** + inorganic Se

[a] Not seleno AA or selenite.

Table 5
Distribution of selenium compounds in plants, fungi, algae, etc.

Compounds	Species
Selenocystathionine (**36**)	*Aspergillus fumigatus* *Aspergillus terreus* *Astragalus pectinatus* *Astragalus praleongus* *Brassica oleracea capitata* *Lecythis ollaria* *Morinda reticulata* *Neptunia amplexicaulis* *Penicillium chrysogenum* *Stanleya pinnata*
Se-Methylselenocysteine (**37**)	*Allium cepa* *Allium sativum* *Allium tricoccum* *Astragalus bisulcatus* *Astragalus crotalariae* *Astragalus praleongus* *Brassica oleracea botrytis* *Brassica oleracea capitata* *Dunaliella primolecta* *Melilotus indica* *Oonopsis condensata* *Phaseolus lunatus*
γ-Glutamyl-*Se*-methylselenocysteine (**38**)	*Allium cepa* *Allium sativum* *Aspergillus terreus* *Astragalus bisulcatus* *Penicillium chrysogenum* *Phaseolus lunatus*
Selenomethionine (**42**)	*Allium tricoccum* *Aspergillus fumigatus* *Aspergillus terreus* *Brassica juncea* *Brassica oleracea capitata* *Melilotus india*
Se-Methylselenocysteine *Se*-oxide (**43**)	*Brassica oleracea capitata*
Selenobiotin (**45**)	*Phycomyces blakesleeanus*
Selenocysteine (**47**)	*Fusarium* sp. *Vigna radiata*
Dimethyl selenide	*Penicillium* sp.
γ-Glutamylselenocystathionine (**40**)	*Astragalus pectinatus*
γ-Glutamylselenomethionine (**48**)	*Allium sativum*
Se-Adenosylselenohomocysteine (**49**)	*Saccharomyces cerevisiae*
Selenocysteic acid (**50**)	*Dunaliella primolecta* *Fusarium* sp.
Se-Methylselenomethionine (**46**)	*Aspergillus fumigatus* *Dunaliella primolecta*
Selenolanthionine (**51**)	*Saccharomyces cerevisiae*
4-Selenouridine (**52**)	*Escherichia coli*
3-Butenyl isoselenocyanate (**53**)	*Stanleya pinnata*
Selenosinigrin (**54**)	*Armoracia lapathifolia* *Stanleya pinnata*
Selenosugars (**55**–**57**)	*Astragalus racemosus*

enzymes are slightly lower for the seleno isologues, and this is balanced by smaller maximum velocities (V_{max}). There are, however, exceptions to this rule. A highly specific selenate reductase has recently been purified from the proteobacterium *Thauera selenatis* (Schroder et al., 1997). Some cystathionine lyases reportedly prefer selenocystathionine (**36**) over cystathionine (McCluskey et al., 1986). Also the key enzyme leading to *Se*-methylated selenocysteine (**37**) and its derivatives, the *S*-adenosyl methionine-dependent selenocysteine methyltransferase, works much less efficiently with, and has a lower affinity for, cysteine. Selenomethionine (**42**) is the major compound in microorganisms like yeast, which is not specialized in selenium utilization.

Se-enriched yeast is the most abundant commercially available source of supplemental Se, selenomethionine being the primary chemical form of Se in yeast. Because manufacturers of Se-enriched yeast do not adhere to a single production and/or quality standard, the form of Se probably varies considerably from product to product. Mutations in ATPS (sulfate adenylyl transferase, EC 2.7.7.4) in the yeast *Schizosaccharomyces pombe* resulted in increased selenate tolerance (Banszky et al., 2003). The selenate resistant phenotype of these mutants was correlated with low sulfate uptake capacity and low ATPS activity.

5.2. Selenium in fungi and plants

Some but not all mushrooms accumulate Se. A survey of 83 species of wild mushrooms reported Se concentrations ranging from 0.01 to 20 mg/kg. *Agaricus bisporus* can accumulate very high concentrations of Se. Other mushrooms that may accumulate Se include *Boletus edulis* and *B. macrolepiota*. Some studies have reported Se from mushrooms to have low bioavailability, and it has also been reported to be present in low-molecular weight compounds that are not selenocysteine, selenomethionine, or selenite.

Both selenites and selenates are taken up by plants and converted to protein-bound selenocysteine (Stadtman, 1996) and selenomethionine, soluble inorganic forms, several free amino acids, and volatile organoselenium compounds.

Plants accumulate varying amounts of Se in different chemical forms; some accumulate Se in direct relationship to the amount available from the soil, whereas others (Se accumulators) may accumulate Se in concentrations many orders of magnitude above that in the soil. Se is present in plants in many different chemical forms that partially dictate the metabolism of Se by the animal that consumes the plant. The Se content and chemical form in plants may be altered by manipulation of plant genetics or by agricultural production conditions (Finley, 2005). S and Se uptake, transport and assimilation pathways in plants exhibit both similarities and differences as observed in Se hyperaccumulator and non-accumulator plant species. Plant bioengineering helps to elucidate the function of sulfate transporters and key enzymes of the S assimilatory pathway in relation to Se accumulation and final metabolic fate, the essentiality of Se in plants and the mechanisms utilized by Se hyperaccumulators to circumvent toxicity (Sors et al., 2005a,b).

Se-enriched plants may be divided into two broad groups (Terry et al., 2000), i.e. selenium accumulators and/or

Table 6
Distribution of selenocompounds in various biological materials

Biological materials	Percentage distribution[a]					
	Selenate	Selenite	**37**, **38**	**42**	**46**	Other[b]
Different vegetables	1–50					
Wheat grain	12–19[c]		1–4	56–83	4–12	4–26
Wheat straw	97[d]					3
Corn				61–64	15–16	20–24
Rice	1–3	5–13		68–81	6–10	19–31
Soybeans				>80		
Grassland legume			10–13	51–70	19–39[e]	
Phytoplankton[f] (15%)	1.0 (0.15)	83 (12)	12.8 (1.9)	3.2 (0.5)		
Astragalus praelongus (95%)	1.4	9	52	37		
Commercial preparation (95%)	0.6	98.7		0.7		
Se-enriched yeast[f] (8.5%)		27 (2.3)	13 (1.1)	59 (5.0)		5 (0.4)
Se-enriched garlic	2–5	8	47–87	1–6	1–13	4–36
Se-enriched yeast	4		6–20	23–63	13–21	13–51
Se-enriched onions			42–55	1–4	7–38	21–35
Se-enriched broccoli florets			63	5	11	21
Se-enriched broccoli sprouts	20		45	12		3
Se-enriched wild leeks (bulbs)	12–25		35–50			1–3

[a] In most cases the percentage distributions were calculated from the areas under the curves of the chromatograms.
[b] Includes **36**, **49**, **51**, **58**, **59**, **60**, and unknown.
[c] Combination of selenate, selenite and **50**.
[d] Mixture of selenate and **50**.
[e] **46** and **60**.
[f] Numbers in parentheses represent the percentage of selenium extracted by aqueous solution.

selenium non-accumulators. Selenium-accumulating plants can be divided into three subgroups: selenite-accumulators (broccoli and cucumber), selenomethionine accumulators (grains such as wheat and mushrooms), and *Se*-methyl selenomethionine accumulators (garlic and onion) (Whanger, 2002).

Most non-accumulator plants contain only moderate foliar Se concentrations, that rarely exceed 100 μg/g dry weight when growing on seleniferous soils (Bell et al., 1992). Yet, a small number of plants, growing on naturally occurring soils containing only 2–10 mg/kg Se, can accumulate well over 1 mg/g dry weight Se, and these plants have been classified as Se hyperaccumulators (Ellis et al., 2004). The largest group of Se-hyperaccumulating plants belongs to the genus *Astragalus* (Fabaceae) (Emerick and DeMarco, 1990). Twenty-five species of *Astragalus* have been characterized as Se hyperaccumulators (Shrift, 1969). Some species can accumulate up to 0.6% of shoot dry weight as Se from soils with 2–10 μg/g dry weight. This is 100–1000 times more Se than found in adjacent non-accumulating plants including other *Astragalus* species (Shrift, 1969; Sors et al., 2005; Pickering et al., 2003).

In these plants, Se is often in methylated forms such as selenocystathione (**36**), *Se*-methyl selenocysteine (**37**), γ-glutamyl-*Se*-methyl selenocysteine (**38**), methyl selenol (**39**), γ-glutamyl selenocystathione (**40**), and selenohomocysteine (**41**). These forms of Se may be safely stored in membrane-bound structures within the plant; Se hyperaccumulators have a relatively small percentage of their total Se sequestered in the protein fractions of the plant. Certain species of *Astragalus* may accumulate in excess of 2 mg Se/g plant tissue, often in forms such as **36**–**41**. Selenocysteine-specific methyltransferase is needed for production of many of these compounds, and insertion of the gene for this enzyme into an Se-non-accumulator *Astragalus* species converts the plant to a Se hyperaccumulator. Recently, this gene has been inserted into *Arabidopsis*, allowing accumulation of **37** and **40**.

Amino acid **38** and its γ-glutamyl derivative are other components of the major pool of seleno compounds in accumulator plants, while selenomethionine (**42**) is the major compound in microorganisms like yeast (see above). Another group of seleno metabolites characteristic of some accumulator plants are the isoselenocyanates and their precursors, the selenosinigrins. Like their sulfur isologues they appear to be common in *Crucifera*. Their biosynthesis has been studied in horseradish and *Stanleya pinnata*. Selenobiotin (**45**) was detected in *Phycomyces* (*Zygomycetae*). Its biological role remains obscure.

Plants absorb Se from soil primarily as selenate and translocate it to the chloroplast, where it follows the sulfur assimilation pathway. Se is reduced (enzymatically and non-enzymatically) to selenide, which reacts with serine to form selenocysteine (**36**). It can be further metabolized to selenomethionine (**42**) and methylated to form products such as *Se*-methyl selenomethionine (**46**). Alternatively, selenocysteine-specific methyl transferase may form *Se*-methyl selenocysteine (**47**), allowing the plant to accumulate large amounts of Se.

S-adenosyl methionine-dependent selenocysteine methyltransferase was discovered in *Astragalus bisulcatus*, a prototype plant selenium accumulator. The closely related species, chick-pea milkvetch *Astragalus cicer*, which is not a selenium accumulator, lacks selenocysteine methyltrans-

ferase under conventional culture conditions. When *A. cicer* is slowly adapted to a selenium-rich substratum, the selenium tolerance is accompanied by the appearance of selenocysteine methyltransferase. Evidently, the ability of specialized plants to methylate selenocysteine more efficiently and to accumulate selenium in the better tolerated *Se*-methylated forms is one of the prerequisites for surviving on seleniferous soils. In accordance with this assumption, **37** and derivatives such as γ-glutamyl-*Se*-methylselenocysteine (**38**) were predominantly detected in typical selenium accumulators of the genus *Astragalus* and other selenium-tolerant plants like *Brassica* and *Allium* species.

Se-enriched garlic contains Se primarily as γ-glutamyl-*Se*-methyl selenocysteine (**38**). Species of *Brassica* that are reported to accumulate Se include: broccoli (*Brassica oleracea*), Indian mustard (*Brassica juncea*), Brussels sprouts (*Brassica oleracea* L.), and canola (*Brassica napus*). *Brassica* spp., especially broccoli and canola, also have been used for phytoremediation, a process that uses Se hyperaccumulators to remove high (potentially toxic) concentrations of Se from soil and/or irrigation water. In a single growing season, broccoli may extract up to 20% of soluble Se from Se-laden drainage water.

γ-Glutamyl-*Se*-methyl selenocysteine **48** is the major selenium compound in natural and selenized garlic, and is an effective carcinogenic agent against mammary gland cancer in rats.

Organoselenium compounds can be used as antiviral and antibacterial agents (Mugesh et al., 2001; Klayman and Gunther, 1973; Shamberger, 1983; Parnham and Graf, 1991).

Using electrophoretic separation (SDS-PAGE) of proteins extracted from Se-75-labelled biomass and ion-pair chromatography coupled with ICP-MS detection, Bryszewska et al. (2005) studied Se-enriched plant biomass to evaluate the ability of rye seedlings to take up and assimilate inorganic Se. The data from the electrophoretic fractionation of proteins and the HPLC separation of Se-species in proteolytic digests revealed a large number of Se-containing compounds in the biomass and showed a complete biotransformation of inorganic Se into organic forms during germination of the rye seedlings. HPLC–ICP-MS analysis of extracts from the plant biomass did not show the presence of selenate or selenite. According to the authors, a combination of different enzymes rather than the commonly used protease should be used for Se extraction from different food types.

Selenium-containing root exudates were investigated in a selenium accumulator plant, Indian mustard (*Brassica juncea*), grown hydroponically and supplemented with selenite (Vonderheide et al., 2006). Selenocystine, selenosulfate ion and several other Se-containing compounds including dimethylselenide were identified in the exudate-containing solution. At neutral pH, fortified selenoamino acids were incorporated into peptide structures, probably due to the action of exuded enzymes.

Zhang et al. (2006) studied Se accumulation in the shoots of two japonica rice (*Oryza sativa* L.) cultivars, differing about three-fold in their ability to accumulate Se in the grain and growing in media with different forms of Se. In the presence of selenite, the shoot Se accumulation by the stronger Se accumulator cultivar was faster and the seedlings absorbed selenocysteine more rapidly than seedlings of the other cultivar. However, when treated with selenomethionine, the lower accumulating cultivar accumulated Se much more than the other. The high Se accumulation rate in seedling shoots of the stronger accumulator may reflect its higher capacity to transform selenite to organic Se compounds and a higher selenite uptake rate.

5.3. Selenium in aquatic organisms

The blue-green alga *Spirulina platensis* has been studied as a possible source of Se/iodide pharmaceuticals. Se in *Spirulina* has been reported to be in a high-molecular weight form. Overall bioavailability of Se from *Spirulina* was reported to be low, but an ultrafiltrable soluble fraction was highly bioavailable. Se-enriched kelp is commercially available as a dietary supplement. *Se*-Methylselenocysteine *Se*-oxide (**43**), which is found in marine algae, tends to spontaneously decompose with the formation of pyruvate and ammonia *via* aminoacrylic acid and methaneselenic acid (**44**). The latter reacts with sulfhydryls or selenols to selenodisulfides and diselenides, respectively.

Recently, some organoselenium compounds have found pharmacological applications as therapeutic agents in the treatment of several diseases.

5.4. Selenium and human health

Selenium-containing supplements are thought to be more effective when the selenium is ingested in an "organic" form, e.g. as selenized yeast (see above), which contains largely selenomethionine (**42**) bound in proteins in addition to many other unknown selenium species. Consumers of such products should be aware, however, of the toxicity of selenium and the possible toxic consequences of overindulgence. Because urine is a major excretory route for selenium, metabolic changes delineating the boundary between essential and toxic concentrations are likely to be reflected in urinary selenium species.

Recent studies of the mechanisms of inflammation in humans (Curran et al., 2005) pointed out an important role of the *SEPS1* gene that encodes SEPS1 selenoprotein that may be relevant to the appearance of several inflammatory diseases such as insulin-dependent diabetes mellitus, celiac disease, atherosclerosis or Alzheimer's disease.

The first compounds demonstrating chemopreventive potential were found in plants such as broccoli and green tea. Today, chemoprevention refers to the use of both natural and synthetic Se compounds to inhibit carcinogenesis. Mammalian selenoproteins play critical roles in many vital cellular functions and are, therefore, essential for disease

prevention (Rayman, 2000). The use of organoselenium compounds for cancer prevention is being explored (Mugesh et al., 2001; Ganther, 1999; Ip, 1998).

5.5. Conclusion

Selenium, an essential micronutrient for plants and microorganisms, has a direct impact on human health and environmental safety. Se supplementation of populations with low or deficient Se intakes may improve health, in populations with adequate intakes it may reduce the risk of cancer. Selenium levels in the body are relevant for protection against chronic degenerative, neurological or neoplastic diseases.

Compounds **37**, **42**, and **47**, which participate in redox reactions, for instance in antioxidant enzymes, are important components of selenium-enriched yeast used as food supplement and therapeutic agent. Organoselenium compounds are promising also as antiviral, antibacterial and antifungal agents and in preventing heart disease and other cardiovascular and muscle disorders. They also exhibit considerable antioxidant activity.

Investigations into selenium metabolism include state-of-the-art methods such as HPLC/ICP-MS in combination with MS/MS. Data on the profile of selenium metabolites will elucidate the element's essential and toxic roles and relate individual Se species with observed health effects.

6. Tellurium

The principal source of tellurium is the anode sludges produced during the electrolytic refining of blister copper. It is also a component of dusts from blast furnace refining of lead. Tellurium is a relatively rare element that has no significant biological role. Tellurium and tellurium compounds are considered to be toxic and need to be handled with care. Organotellurium compounds damage cells, e.g., by oxidizing sulfhydryl groups and depleting endogenous reduced glutathione in a variety of tissues. The role of tellurium in biological systems has been reviewed by Taylor (1996). *E. coli* cells, expressing the genes localized in a chromosomal DNA fragment from *Geobacillus stearothermophilus* V, produced volatile organotellurium compounds (Swearingen et al., 2004) including dimethyl telluride, dimethyl ditelluride and two new compounds, methanetellurol (CH_3TeH) and dimethyl tellurenyl sulfide (CH_3STeCH_3). Chasteen and Bentley (2003) reviewed the processes leading to biomethylation of selenium and tellurium in microorganisms and plants.

7. Astatine

It has been estimated that the whole Earth's crust contains less than 44 mg astatine and this element can thus be considered one of the rarest naturally occurring elements on Earth. All isotopes of this radioactive element have short half-lives and are products of several radioactive decay series. Because of the very low half-life of its isotopes, the radioactive astatine has no significance for living systems.

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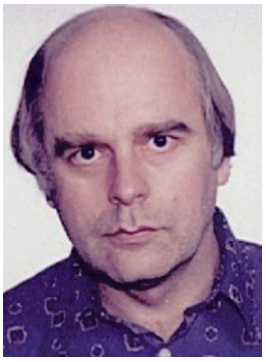

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