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Review

Natural occurrence of boron-containing compounds in plants, algae and microorganisms

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Abstract

Discovery of naturally-occurring boron compounds, all ionophoric polyketide macrodiolide antibiotics with a single boron atom critical for activity, established at least one biochemical role of boron. This review focuses primarily on presence and distribution of boron-containing compounds in vascular plants, marine algal species, and microorganisms.

Keywords: Plants; Algae; Microorganisms; Boron-containing compounds

1. Introduction

After the discovery in 1910 [1] that boron is one of the essential microelements for higher plants [2], its biological role has been the subject of a number of studies (see reviews [3–7]). Boron is a micronutrient element required for growth and development of vascular plants, marine algae and algal flagellates, diatoms and also cyanobacteria [8].

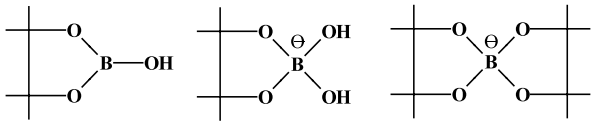
2. Possible functions and properties

Biological and physiological functions for boron and boron-containing compounds are well established ,nevertheless, many questions still remain to be answered [8–12]. It is known that boron is absorbed from soil solution by roots mainly as the undissociated boric acid (H_3BO_3, $pKa_1 = 5.8 \times 10^{-10}$ at 25 °C) and accumulated in stalks, roots, shoots and also cell walls of many plants [11]. Dissociation of boric acid in water is indicated below:

$$H_3BO_3 + H_2O = H_4BO_4^{-1} + H^+ \quad (pK - 9.23)$$

In addition, boron may be of importance for maintaining the structural integrity of plasma plant cells membranes. This function is likely related to stabilisation of cell membranes by boron association with some membrane constituents [8,12]. The formation of boron-containing complexes with *cis*-diol configurations in certain plant species plays an important role in boron transport [6,8,9,11–13]. Thus boric acid reacts with alcohols forming boron esters (**1**) and/or neutral *cis*-diol monoborate esters (**2**) or monoborate complexes with sugars (**3** and **4**) [14].

$$B(OH)_3 + 3ROH = B(OR)_3 + H_2O \quad (1)$$



(2) (3) (4)

Also boric acid can form borate complexes with organic acids such as malic acid neutral borate complex (**5**), monomalic acid borate complex (**6**), and the

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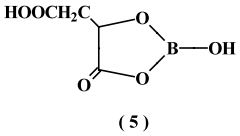
bis(malic acid) borate complex (**7**). These boron-containing compounds were found in apple juice and wine [15,16].



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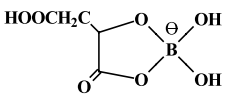

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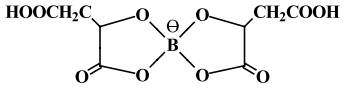
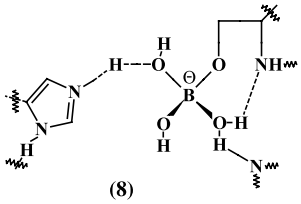


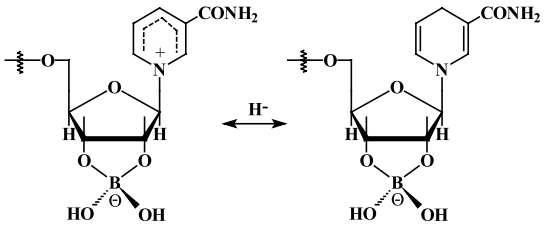
(7)

Different enzymes of plants, microorganisms, animals and humans could be reacted with boron compounds resulting in stimulation, stabilisation and/or inhibition. For instance, the enzyme urease immobilized on a membrane was found to be inhibited by boric acid [17]. Borate buffer inhibited succinic dehydrogenase of *Neurospora,* phosphoglucomutase of pea seeds [18], and also alcohol dehydrogenase of yeast [19]. Borate and boric acid are inhibitors for a variety of enzymes systems in animals [20–22]. This inhibition is attributed to borate occupying the active site, as for example, the active site of a serine protease (**8**) [20].



(8)

In plants, boron deficiency releases the inhibition of 6-phosphogluconate- and of glucose-6-phosphate dehydrogenases, resulting in increased phenols production [23–28]. These competitive inhibitions possibly involve ribityl hydroxyls of the coenzyme NAD/NADH system and borate (**9**) [29,30].



NAD-Borate NADH-Borate

(9)

Blevins and Lukaszewski [31] have demonstrated that boric acid inhibits allantoate amidohydrolase, a Mg^{+2}-containing enzyme. This result suggested that one of many boron functions in plants is regulation of metal-containing enzymes. It is important to recognize, however, that the capacity for boron to influence metabolism does not prove that these reactions are biologically relevant at normal cellular boron concentrations.

3. Detection boron in biological samples

Recently, many published methods of detection of boron in natural samples were reviewed by Sah and Brown [32]. Biological samples are commonly decomposed by dry ashing, wet ashing, and/or microwave dissotution and detected by spectrometric methods. Boron may be extracted as organic boron complexes, i.e. boron-2-ethyl-1,3-hexanediol complex of boron into chloroform or benzene [33,34], 2,4-dinitro-1,8-naphalenediol complex of boron in toluene [35] and/or 2,4-dimethyl-2,4-octanediol boron complex into isopentanol [36]. HPLC may be used for separating the ionic boron complexes with chromotropic acid [37] or H-resorcinol [38]. Some of nuclear reaction analytical methods have been reported for boron measurement [32] while a more comprehensive method is ^{11}B-NMR. This method has been successfully used for detecting boron in marine algae [39] and plants [32,40]. Fig. 1 demonstrates the occurrence of boron-containing complexes in some seaweeds, determined using ^{11}B-NMR spectrometry.

Van Dongen et al. [41] have recently used boron-complexes of saccharides to determine the natural isotopic abundance of intact plant monosaccharides

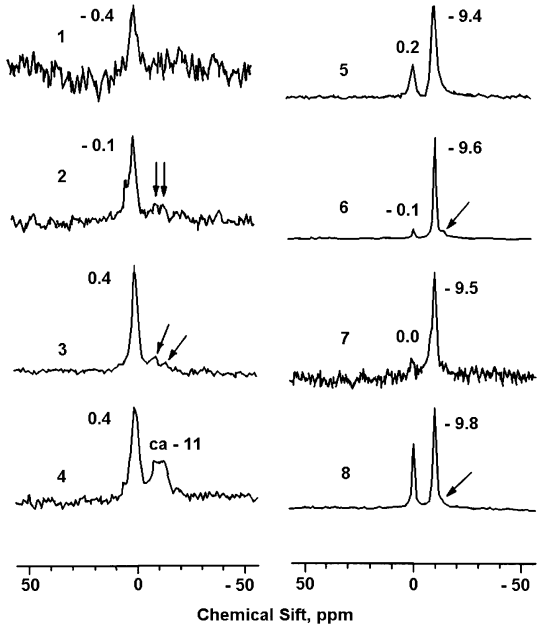


Fig. 1. Comparative ^{11}B-NMR spectra of some marine algae. Red algae, *Gloiopeltis tenax* (1), *Grateloupia turuturu* (2), Green algae, *Ulva fasciata* (3), *Ulva pertusa* (4), Brown algae, blade of *Undaria pinnatifida* (5), stripe of *Undaria pinnatifida* (6), blade of *Laminaria japonica* (7), stripe of *Laminaria japonica* (8). The spectra were ploted using the same *Y*-axis gain. Small peaks are indicated by arrows [39]. Adapted by authors.

(arabinose, xylose, fucose, fructose and glucose). The method is rapid, does not involve isotopic fractionation during the methylboronic derivatization stage, and gives more precise δ^{13} C values than all other methods. The method was successfully used to determine the δ^{13} C value of glucose of the freshwater alga *Scenedesmus communis* [41].

4. Distribution in plants

There are many different biological compounds that can form complexes with boron, both in the cytoplasm and in the cell wall. Compounds capable of complexing with boric acid include sugars or their derivatives, phenols, organic acids and some polymers [42,43]. Yamaguchi et al. [44] reported that boron-polysaccharide complexes were solubilized from cell walls of tomato leaves. Later these complexes were isolated and characterizated from radish (*Raphanus sativus*) roots [40]. The complex had a molecular weight of 7.5 Kda and contained boron (0.232%), uronic acid (52.0%) and neutral sugars (32.4%). According to ^{11}B-NMR analysis, the authors suggested that the boron was present as a tetravalent 1:2 borate-diol complex [40]. Boron-rhamnogalacturonan-II (BR-II) was isolated from radish roots. ^{11}B-NMR was used to eastablish that BR-II boric acid links with two rhamnogalacturonan-II chains, which include apiose, aceric acid, 2-O-methylfructose, and 3-deoxy-D-manno-2-octulosonic acid, rhamnose, galactose, and arabinose [45]. BR-II complex was isolated from cell walls of sugar beet (*Beta vulgaris*) [46]. ^{11}B-NMR spectroscopy showed that the boron was present as a tetrahedral borate-diol diester. The polysaccharide moiety contained 2-O-methylfucose, rhamnose, fucose, 2-O-methylxylose, arabinose, apiose, galactose, aceric acid, galacturonic acid, and glucuronic acids residues [46]. A ^{11}B-NMR spectrum of the BR-II complex from sugar beet cell walls of the same boron-complex isolated from brown algae is shown in Fig. 1(7)

Partially acid hydrolyzed BR-II complex from sugar beet (*B. vulgaris*) were characterized and consisted of two disaccharide moiety: α-L-Rha*p*-(1→5)-D-Kdo and α-L-Ara*f*-(1→5)-Dha, an aceric acid-containing oligosaccharide, and a 2-O-Me-Xyl-containing oligosaccharide, in addition to partially methyl-esterified α-(1→4)-oligogalacturonides were determined [47]. BR-II contains at least 11 different monosaccharides, including the following seldom-observed sugars, apiose [Apt; 3-C-(hydroxymethyl)-D-glycerol-aldotetraose], 2-0-Me-L-fucose, 2-0-Me-D-xylose, and aceric acid (AceA; 3-C-carboxy-5-deoxy-L-xylose). The monosaccharide constituents of BR-II complexes are interconnected by at least 100 different glycosidic linkages [48]. 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 apiose-containing oligosaccharides [49–51] and two 3-deoxy sugar containing disaccharides, that is, α-L-Rha*p*-(1→5)-D-Kdo [52] and β-L-Ara*f*-(1→5)-D-Dha*p* [53]. BR-II complex isolated from a Driselase digest of bamboo (*Phyllostachys edulis*) shoot cell walls has almost the same structure as that of sugar beet cell walls [54]. Cell walls of *Cryptomeria japonica* polysaccharides contained the glycosyl residues of BR-II, besides small amounts of the glycosyl linkages of BR-I [55]. A borate ester cross-linked dimer BR-II has been isolated from sycamore, pea and wine [41]. Major glycosyl residues determined in the BR-II complexes were galactose (37–51%), rhamnose (11–16%) and arabinose (10–13%). Major monosaccharide units isolated from polysaccharides of *Pinus radiata* were xylose (33–41%) and glucose (16–32%) [56]. The boron-containing pectic polysaccharide from Driselase digest of akamatsu (*Pinus densiflora*) has the sugar composition and glycosyl linkage similar to BR-II [57]. Ishii et al. [58] studied the composition of glycosyl residues of mono- and dimeric polysaccharides linked by glycosyl bonds in RG-II from control and boron deficient plants were similar. The major glycosyl residues identified were GalA (43%), Gal (10%) and Ara (9%) in dimmer RG-II, and GalA (38%), Ara (12%) and Gal (9%) [58].

Boron-containing polyol complexes have been isolated and characterized from the phloem sap of celery (*Apium graveolens*) and extrafloral nectar of peach (*Prunus persica*) [59]. In celery the direct analysis of untreated phloem sap showed that boron is present in the phloem as the mannitol-boron-mannitol complex. Molecular modeling further predicted that this complex is present in the 3,4,3′,4′ *bis*-mannitol configuration (Fig. 2). In the extrafloral nectar of peach, boron was present as a mixture of sorbitol-boron-sorbitol, fructose-boron-fructose, or sorbitol-boron-fructose. The authors suggested that the isolation of the mannitol-boron-mannitol complexes from the phloem of celery and the presence of the sorbitol- and fructose-boron complexes in peach provide a mechanistic explanation for the observed phloem mobility of boron in *A. graveolens* and *P. persica* [59]. These complexes are the first soluble boron complexes isolated from higher plants and functions not yet established. A requirement for borate in crosslinking plant cell wall polysaccharides was recently reported [60].

Investigation by the van Bekkum group and others, of borate ester formation of mono- and dimeric polysaccharides indicated the most stable complex to occur with furanoidic *cis*-1,2-diols [[61] and references cited]. Recently, Benner and Klüfers [62] using a combined X-ray and NMR method, reported for the first time two structures of furanoidic *cis*-1,2-diol borate esters: 1,4-anhydroerythriol (**10**) and methyl β-D-riboduranoside (**10a**) boron-containing complexes.

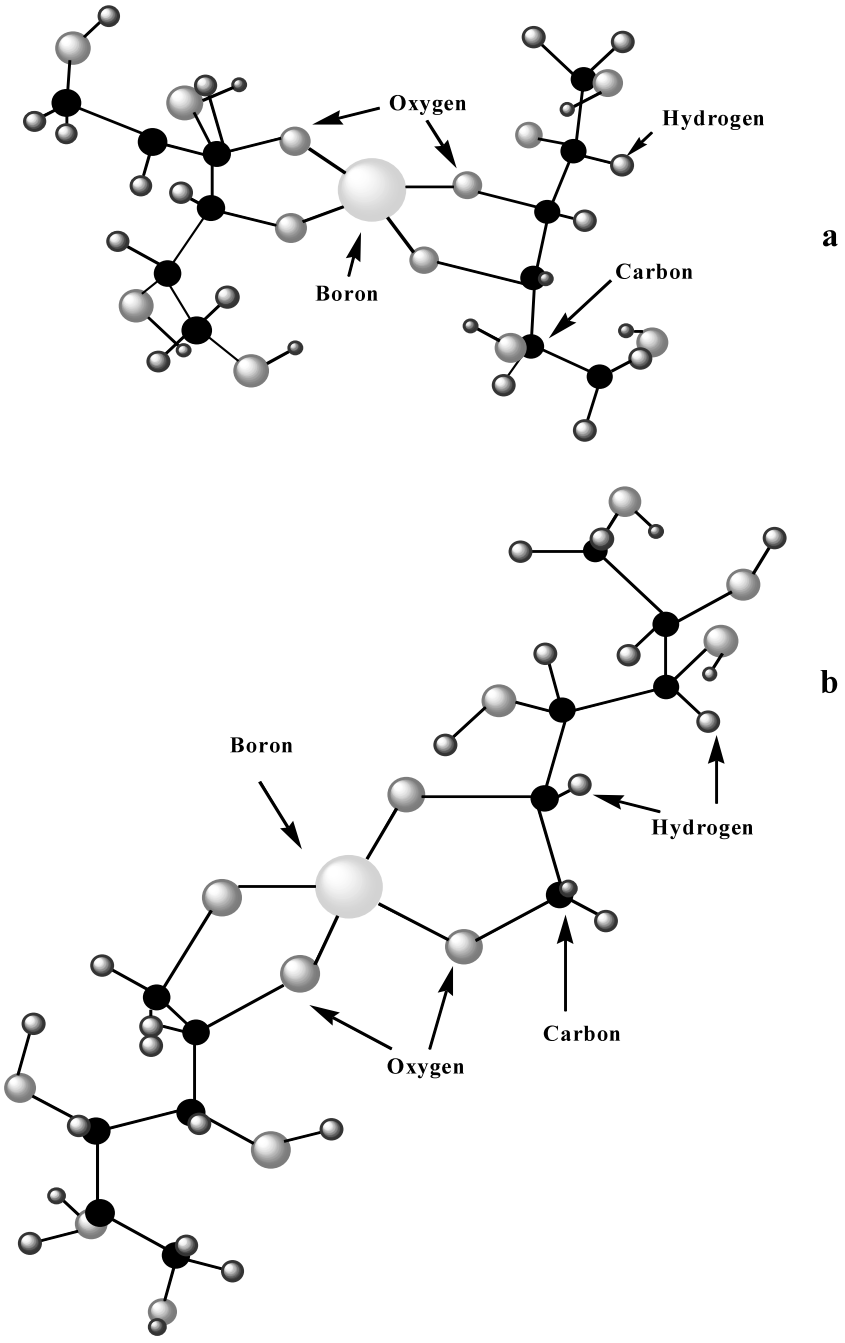
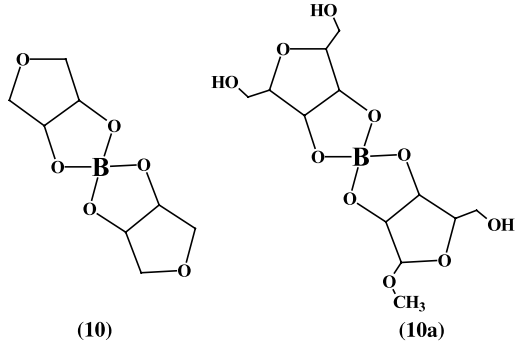


Fig. 2. Molecular modeling and predicted three-dimensional configuration of 3,4,3′,4′ (a) and 1.2 1,2 bis-mannitol borate complexes isolated from *Apium graveolens* and *Prunus persica* [57]. Adapted by authors.



RG-II is a remarkable molecule (Fig. 3). It is composed of eleven kinds of sugar monomers. At least 21 enzymes are dedicated to the construction of all the linkages between the sugar residues. This molecule must adopt a well-defined three dimensional conformation with boron atom in center of RG-II.

One approach for determining the function of boron in plant cell walls is to compare the responses to boron deficiency of growing plant cells that are dividing and synthesizing primary cell walls with those of growth-

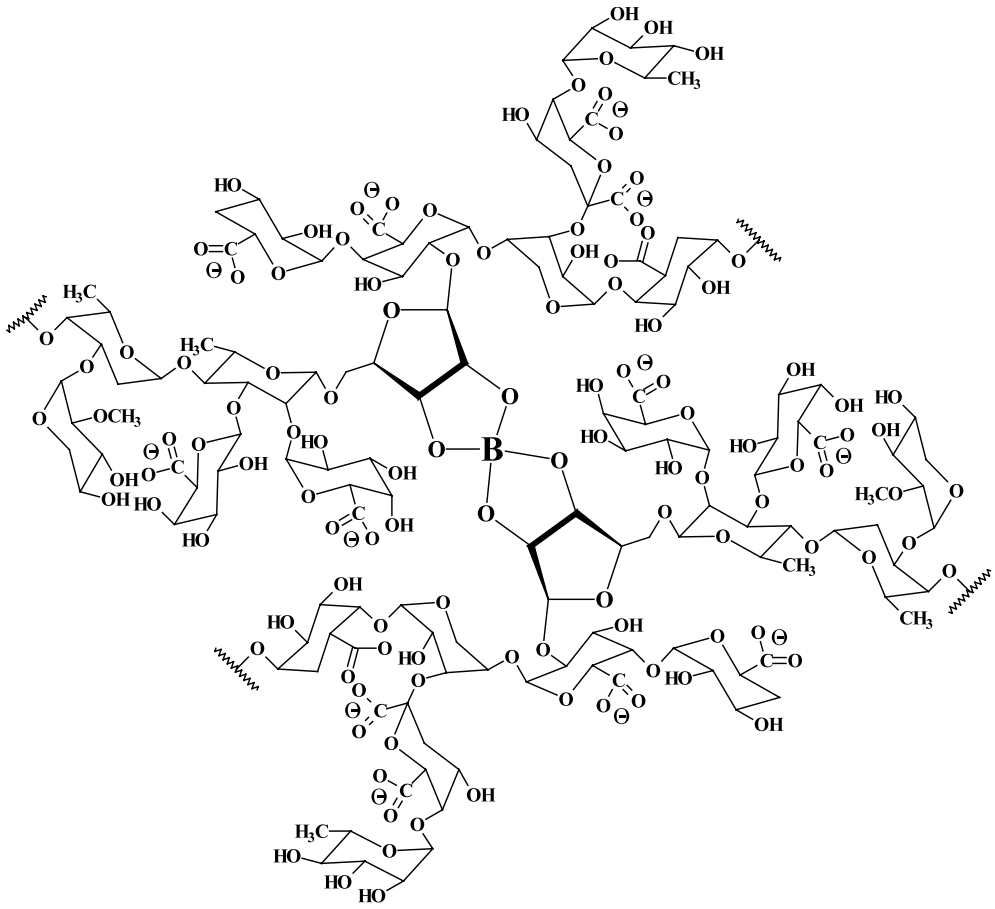


Fig. 3. The central part of boron containing dimeric polysaccharide complex known as RG-II with missing links. It is present in the cell walls of all higher plants [73]. Adapted by authors.

limited plant cells in which the synthesis of primary cell walls is negligible. Already in 1923 Warington [2] reported that boron deficiency caused alterations in legume plants under N_2-fixing. Later, more evidence showing the essential requirement of boron in nodulation were described in several publications [63–66]. The interaction between Ca and boron seems to be at the cell wall-membrane level, but the mechanism involved and the effects of this interaction on N_2-fixation in legumes are still not clear. Literature reports deal with either B or Ca, but very few discuss both elements simultaneously [67]. Yamagishi and Yamamoto [65] have reported strong alterations in N_2-fixation in soybean plants with a low boron supply. In relation to pea plants [63], a number of papers have contributed to the understanding of the necessity of boron in nodulation [66,68], where the role of B strongly appeared in relation to nodule cell walls [65], as was demonstrated in plant cell walls [45,70]. Recent results [67] showed that a high supply of Ca^{+2} could induce boron mobilisation from root to shoot in *Pisum sativum,* and the high boron requirement in pea plant nodules may explain the low nitrogenase activity found.

The cell wall is a complex molecular entity made of polysaccharides, proteins, enzymes, boron, calcium and water that has the ability to self-assemble [71]. Specific glycoproteins which fix boron to the walls of nodule endodermis have been reported [69,72]. These proteins, when bound to the walls by boron ester links, increased the resistance to gas diffusion in nodule. The interactions of boron and hydroxyproline/proline-rich proteins between themselves and with other wall components are still unknown, as is how these wall components are assembled. The possible functions of cell wall proteins are based on repetitive sequence, localization in the plant body, and the general morphogenetic pattern in plants. The evidences found suggests another type B-complex with proteins [69,72,73].

5. Distribution in algae

Various species of seaweed add much to the quality of the traditional food of people in many countries and there for they have become the subject of much attention [74]. Many biological active components were isolated and identified from macrophytic algae such as terpenoids [75,76], halogenated fatty acids [77,78], and unusual betaine ether lipid compounds [79,80]. Kato et al. [81] and Rozentsvet et al. [82] have also described the distribution of these compounds in selected species of vascular plants and marine algae. Phycocolloids, which are polysaccharides, have the ability to give viscosity, gel strength and stability to aqueous mixtures, solutions and emulsions [83,84]. The principal phycocolloids are the alginates (alginic acid salts) from brown algae (Phaeophyta) and the sulphated galactans [85–87], agars and carrageenans, from red algae (Rhodophyta) [88,89].

Recently oligosaccharides [90–93] and boron-containing complexes were reported from marine green algae (Chlorophyta) [94]. The NMR spectroscopic analysis of autohydrolysate fragments obtained from the gel-forming water-soluble cell-wall sulphated polysaccharides from the green seaweed *Ulva* sp. allowed the identification of two major repeating units in ulvan. These were the aldobiouronic acids (1→4)-β-DGl*cp*A-(1→4)-α-L-Rha*p* 3-sulphate and (1→4)-α-L-Ido*p*A-(1→4)-α-L-Rha*p* 3-sulphate that were given the name ulvanobiouronic acid 3-sulphate A and B, respectively. Boron complexes were observed at pH 9 with ulvanobiouronic acid A. These results indicate that the ring hydroxyl groups of the major repeating structures which contain the rarely encountered iduronic acid in plant polysaccharides are probably not involved in the boric acid fixation step during the gelation of ulvan [94].

Free and complex forms of accumulated borate in marine green (*Ulva fasciata* and *Ulva pertusa*), brown (*Laminaria japonica* and *Undaria pinnatifida*) and red algae (*Gloiopeltis tenax* and *Grateloupia turuturu*) were identified by ^{11}B-NMR [39]. The NMR spectra of green and red algae showed boric acid peaks mainly. In contrast, brown algae gave two distinctive peaks predominantly borate containing diesters. To identify the moieties coupled to borate. Boron-containing complexes with compounds containing vicinal hydroxy groups, such as mannitol, laminarin and alginic acid were reported [39]. Each spectrum of all of the examined macrophytic marine algae showed a peak at approximately 0 ppm which was assigned to boric acid (see Fig. 1). In the spectra the red alga *G. turuturu* (Fig. 1(2)) and the green alga *Ulva fusciola* (Fig. 1(3)) two small peaks were observed in the range of −9 to −15 ppm in addition to boric acid peaks. Green alga *U. pertusa* afforded only the broad peak at approximately 11 ppm other than the one at 0 ppm (Fig. 1(4)). The NMR spectra of brown algae were quite different from those of red and green algae. Boron exists in at least three forms in the stipe and two forms in the blade of the brown algae. An intense peak appeared at approximately 10 ppm in each spectrum measured for both *U. pinnatifida* and *L. japonica* (Fig. 1(5–8)) independent of the moiety. Of the four spectra recorded, those of the stipes had small shoulder peaks accompanying the predominant peaks (Fig. 1(6 and 8)). These signals at approximately 10 and-14 ppm correspond to the borate diester forms and monoester forms, respectively, according to the assignment spectra in higher plants [15]. The brown algae contain diesters specifically, while boric acid is the dominant species in the red and the green algae. The results indicated that mannitol forms the main boron diester complexes. Fresh brown algae, therefore, contain large amounts of boron-carbohydrate complexes as do some higher plants [39]. The structures of boron-containing complexes from many seaweeds have still not determined.

The extracellular matrix polysaccharides of marine algae exhibit unique structural features [95]. They are made of a variety of carboxylated and/or sulphated, linear or branched polysaccharidic units such as agars and carrageenans (red algae) and consist of D-galactose residues linked by alternating α-1→3 and β-1→4 linkages [96]. Alginates are one of the main polysaccharides of brown algae and consist of β-1,4-D-mannuronic acid units [96], whereas ulvan is the main polysaccharide of green alga *Ulva* spp. [92,94]. Several recent investigations indicate that oligosaccharide signalling occurs in marine plants, algae and seaweeds and that many concepts derived from the study of host-pathogen interactions in terrestrial ecosystems could be applied to the distant lineages found in the sea [96,97]. Also the oligosaccharide signals in pathogen recognition and defence reactions in marine algae shine new light on the ecology of their interactions with associated microorganisms [96,97].

6. Distribution in microorganisms

Cyanobacteria produce a number of different biologically active peptides with highly modified amino acid residues [98,99] and cyclic hexapeptides containing cyclically modified amino acids [100–102].

Four modified cyclic hexapeptides were isolated along with the known antibiotic, borophycin (**11**), from litophytic cyanobacterium *Nostoc spongiaeforme* var. *tenue* (Nostocaceae) [103]. Potent cytotoxin, borophycin (**11**), also isolated from lipophilic extract of marine cyanobacterium *Nostoc linckia* [104].

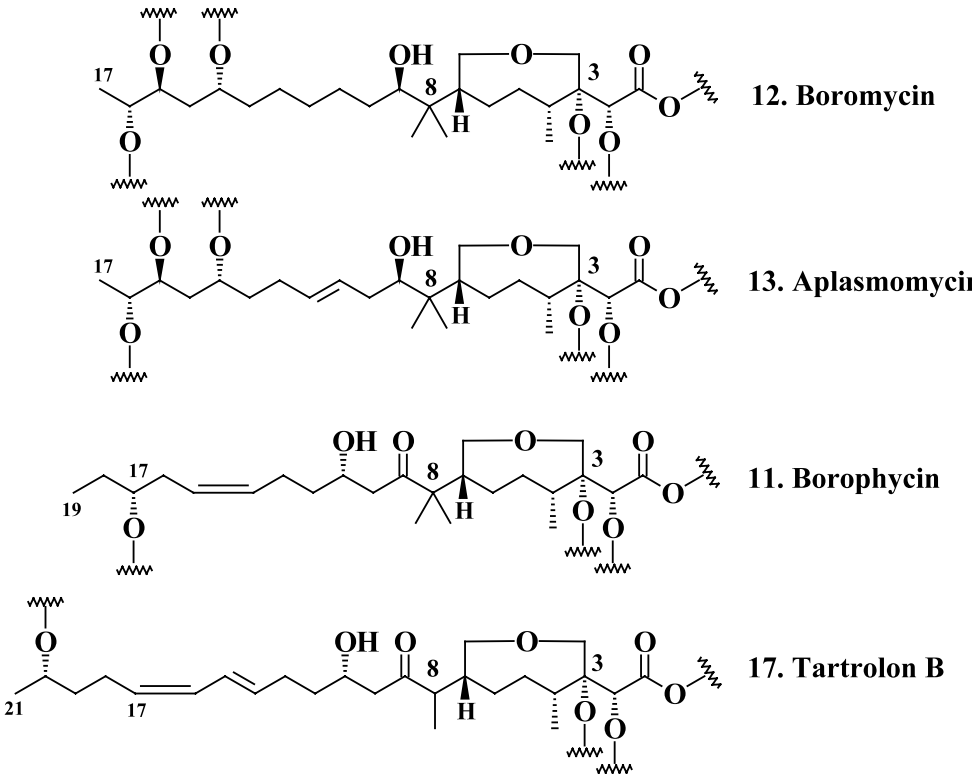
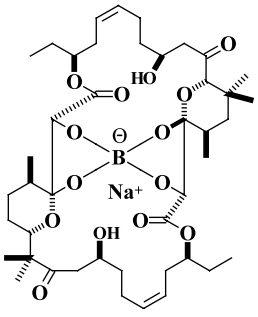


Fig. 4. Comparative carbon skeleton of polyketide chains included in structures of boron-containing complexes isplated from streptomycetes, cyanobacteria and myxobacteria: borophycin (11), boromycin (12), aplasmomycin (13), and tartolon B (17).



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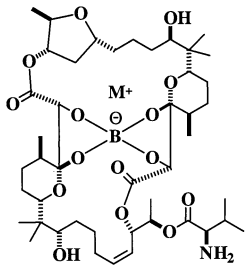

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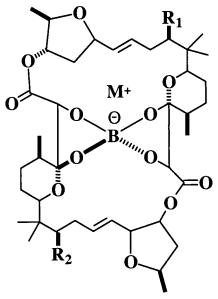


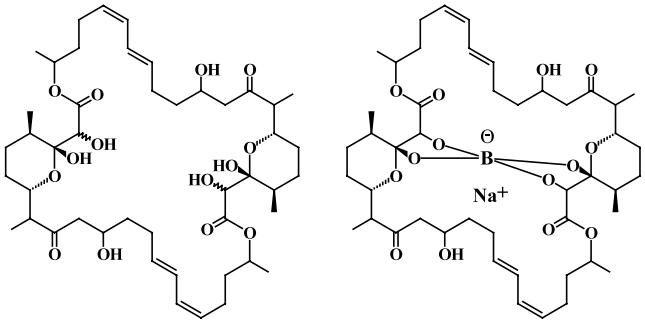
13. R_1 = OH, R_2 = OH
14. R_1 = OH, R_2 = OAc
15. R_1 = OAc, R_2 = OAc

Boromycin (**12**), was first isolated from an African soil sample containing *Streptomyces antibioticus* [105,106]. Aplasmomycin (**13**) which was originally isolated from *Streptomyces griseus,* found in a shallow sea sediment [107], differs from boromycin by having two chemically identical subunits surrounding the borate complex. *S. griseus* produces several variations of aplasmomycin and the series has been designated as aplasmomycins A, B, and C (**13**, **14**, **15**). These natural antibiotics are unique as the only known metabolic products containing the element boron. These seminal investigations are due mainly to the Floss group [108–113] who contributed much to the study of the biosynthetic origins of these molecules.

Aplasmomycin (**13**) was first isolated from a broth cultivated with a marine isolate of actinomycete *Plasmodium berghei* and its structure elucidated by Nakamura et al. [114]. Aplasmomycins B (**14**) and C (**15**) are produced by a strain belonging to *S. griseus* [115].

Novel boron-containing antibiotics, named tartrolons A (**16**) and B (**17**), were isolated from gram-negative eubacteria which live in soil and related habitats [116,117], *Sorangium cellulosum* [118–120]. Absolute configuration and biosynthesis of tartrolon B (**17**) were determined and investigated by Schummer et al. [120]. The biosynthesis of tartrolon B (**17**) is closely related to boromycin (**12**) and aplasmomycin (**13**). But

with respect to the origin of the starter unit it is more closely related to that of borophycin (**11**). These new boron-containing complex tartrolon B (**17**) and also previously isolated boromycin (**12**), aplasmomycin (**13**), and borophycin (**11**) are polyketides and have the same boron-binding substructure C_1–C_7 in each half of the symmetric molecules (Fig. 4).



(16) (17)

Due to a favorable conformation of all macrocycle boron-containing compounds (**7**, **8**, **11**–**13**,**15**), four hydroxy groups of these substructures are idealy positioned to form a Boeseken complex [42] with boron [120]. Recently Berger and Muzler [121] described for the first time a total synthesis of tartrolon B (**17**).

According to cited references boron is not only found in trace amounts in plants, algae and microorganisms but also as a constituent of some antibiotics (**11**–**15**, **17**) [118–120].

A novel AI-2 furanosyl borate diester complex (**20**) was originally identified in the bioluminescent marine bacterium *Vibrio harveyi* as one of two autoinducers that regulate light production in response to sell density [122,123]. Many groups of Gram-positive and Gram-negative bacteria contain enzyme synthase for the synthesis of AI-2 [124]. AI-2 is produced from S-adenosylmethionine in at least three enzymatic steps [125,126]. In the final stage 4,5-dihydroxy-2,3-pentanedione (DPD) (**18**) is converted to the cyclic form of DPD, which is named pro-AI-2 (**19**), and can react with borate to form a cyclic borate diester AI-2 (**20**). The boric acid required for this reaction is widely available in the biosphere. AI-2 has been proposed to serve as a 'universal' bacterial quorum-sensing signal containing boron for inter bacteria community communication [127]. Stephan Winans [128] has termed this '*Bacterial Esperanto*', a novel language between cell-cell communications in bacteria. At least one cyanobacterium also communicates via oligopeptides [129]. In contrast, most signaling in proteobacteria is accomplished using *N*-acylhomoserine lactones [130]. However, earlier studies of AI-2, first discovered in the bioluminescent marine bacterium *V. harveyi*, suggested that it was unlikely to resemble any of these molecules [127,128].

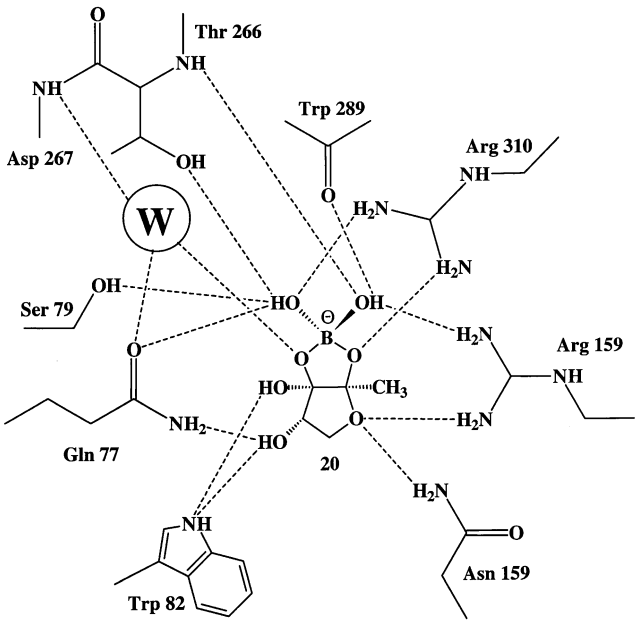
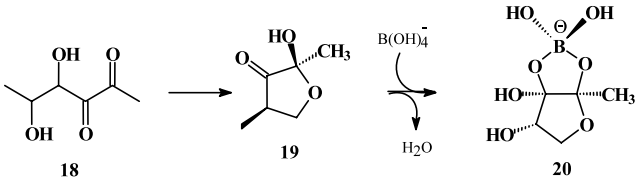


Fig. 5. AI-2 and hydrogen bond network that stabilizes Boron complex in the sensor protein LuxP binding site.



The proposed AI-2 structure contains two fused five-membered rings stabilized within the sensor protein LuxP binding site by numerous polar interactions (Fig. 5) [127].

For the last 50 years there have been other incentives to incorporate boron into different biologically active molecules [131], particularly for medicinal application as boron neutron capture therapy of brain tumors [132,133]. Other methods of synthesis and applications of boron-containing analogues of biomolecules or boron compounds having of biological interest have been observed in some recent reviews [131,134–139].

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