

Melatonin, an underestimated natural substance with great potential for agricultural application

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Abstract Melatonin (MEL) was thought to be only a neurotransmitter found in vertebrates until its detection in other organisms including plants. Although the number of publications on MEL function in plants is expanding, the knowledge of this subject is still insufficient. Among many functions which MEL performs in plants, its role as an antioxidant and a growth promoter is most supported by experimental evidence. This compound is an independent plant growth regulator and it may mediate the activities of other plant growth regulators. Due to its antioxidant properties MEL may also stabilize cell redox status and protect tissues against reactive oxygen and nitrogen species which accumulated under stressful environment. Some researchers propose that MEL could be used to improve the phytoremediation efficiency of plants against different pollutants. In this paper we show that exogenous MEL applied into the seeds could be a good biostimulator improving not only seed germination, seedling/plant growth but also crop production especially under stress conditions. We also believe that this compound can increase food quality (the aspect of functional food) and may improve human health. Since MEL is inexpensive and safe for animals and humans its application as a biostimulator could be a good, feasible and cost-effective method useful in agriculture.

Keywords Abiotic stress · Biostimulators · Melatonin · Seed priming

Introduction

Melatonin (MEL) was isolated in 1958 from the bovine pineal gland by Aaron Lerner and co-workers and its structure was identified as N-acetyl-5-methoxytryptamine. Initially, it was thought that MEL occurred only in animals, but an article in Science (1991) changed this view since authors discovered this substance in the photosynthesizing dinoflagellate *Lingulodinium polyedrum* (present name *Gonyaulax polyedra*). This information has inspired scientists to search for MEL in other autotrophic organisms including higher plants. MEL was first detected in 1995 in mono- and dicotyledon edible plant families (Dubbels et al. 1995; Hattori et al. 1995). Indoloamine is currently understood an ubiquitous and conserved compound, found in evolutionarily distant organisms: bacteria, mono- and multicellular algae, fungi, higher plants, invertebrates and vertebrates (Posmyk and Janas 2009).

In vertebrates MEL is mainly produced by the pineal gland and secreted into the blood stream in a rhythmic manner. MEL is an animal hormone involved in the regulation of physiological processes, including circadian rhythm and photoperiods (Reiter 1991a, b; Stehle et al. 2011). In animals and humans, MEL has been identified as a remarkable molecule not only signaling for seasonal changes but also promoting immunomodulation and possessing cytoprotective properties.

Melatonin in plants

A lot of experimental evidence indicates that the path of MEL biosynthesis is similar in different organisms. L-tryptophan is a precursor of MEL both in animals and plants. In rice plants tryptophan is converted to melatonin

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via tryptamine but not 5-hydroxytryptophan as in animals in the following process: tryptophan decarboxylase (TDC) converts tryptophan to tryptamine which is catalyzed to serotonin by tryptamine-5-hydroxylase (T5H), next serotonin *N*-acetyltransferase (AANAT) catalyzes conversion of serotonin to *N*-acetylserotonin, and this is changed to MEL by *N*-acetylserotonin *O*-methyltransferase (ASMT). Genes of TDC, T5H and ASMT have been cloned and expressed in rice while gene of AANAT has not been characterized in plants yet (Kang et al. 2009; Park 2011, Park et al. 2013a). It is suggested that in plants the pathway of this indoleamine can be more complex than it was thought earlier (Park et al. 2012). Indolyl-3-acetic acid (IAA), an auxin commonly occurring in plants, is also derived from *L*-tryptophan (Posmyk and Janas 2009).

MEL levels differ not only from species to species, but also among varieties of the same species. The reason may be a variable amount of MEL under different environmental conditions (especially stresses), plant developmental stages but also due to the use by scientists various extraction methods and determination techniques (Dubbels et al. 1995; Hattori et al. 1995; Baghurst and Coghill 2006; Reiter et al. 2007; Stürtz et al. 2011). Moreover there also important genetic traits and the type of tissue examined.

This compound was found in many organs of higher plants: roots, stems, leaves, flowers, fruits and seeds at concentrations usually ranging from picograms to micrograms in per gram of tissue (Garcia-Parrilla et al. 2009).

Phytomelatonin has been identified and quantified in more than 140 different plants and plant products (Posmyk and Janas 2009; Murch et al. 2009b; Tan et al. 2012a; Fernandez-Mar et al. 2012). Some crop plants such as *Graminae* (rice, barley, sweet corn, oat, tall fescue) exhibited high content of this indoleamine (Hattori et al. 1995). MEL was discovered in various wild perennial (Zohar et al. 2011) as well as in medicinal plants, e.g., *Hypericum perforatum* L. and others commonly used in Chinese traditional medicine (Murch 1997; Chen et al. 2003). The high level of this compound was found in flower buds of *Datura metel* L. but it decreased following the floral development (Murch et al. 2009a). MEL was found also in fruits such as strawberries, kiwis, pineapples, bananas, apples and in grapes (Hattori et al. 1995; Iriti et al. 2006; Sae-Teaw et al. 2013) as well as tart cherries (Manchester et al. 2000) and tomatoes (Van Tassel and O'Neill 2001; Okazaki and Ezura 2009). This may be related to their high sensitivity to environmental stresses including UV radiation during buds development and plant growth (Murch et al. 2009a).

High content of MEL ($115.25 \mu\text{g g}^{-1}$ f.w.) was also found in freshly harvested seeds of *Coffea canephora* P ex Fr. (Ramakrishna et al. 2012a, b) and in seeds of edible plants such as anise, coriander, flax, alfalfa, fennel,

sunflower, black and white mustard and many others (Manchester et al. 2000). It may suggest that in seeds this compound provides antioxidative defense in a relatively dry system which cannot be up-regulated. Thus, MEL may be in seeds the essential compound protecting germ and reproductive tissues of plants from harmful environmental conditions (Manchester et al. 2000; Murch et al. 2009a).

Generally MEL levels in plants are higher than in animals. Perhaps because in plants unfavorable environmental conditions can be avoided only by its metabolic modification not by escape. Moreover tryptophan (MEL precursor) availability in plants is theoretically unlimited—they are able to produce aromatic amino acid via shikimic acid pathway—in contrast to animals, which are devoid of this metabolic route and must intake of this amino acid from the diet (Yao et al. 2011).

Although the number of publications on MEL function in plants is growing, understanding is still poor but there is lack of data concerning transport of this molecule in plants as well as its subcellular and histological location.

Exogenous MEL is absorbed by plant roots as in the water hyacinth (*Eichornia crassipes* L.) and delivered to leaves where its level dramatically rises (Tan et al. 2007b). Burkhard et al. (2001) reported presence of MEL in two varieties of cherry (*Prunus cerasus* L.) and suggested that MEL could be synthesized in fruit but the compound may also be picked up from soil by roots and transported to plant organs including fruit. It cannot be excluded that MEL found in plants come from decomposing soil microorganisms such as bacteria, fungi and unicellular algae (Tan et al. 2012a; Muszyńska and Sułkowska-Ziaja 2012). Not only roots are capable of absorbing MEL in dose-dependent manner but also cotyledons of lupin (*Lupinus alba* L.), leaves of barley (*Hordeum vulgare* L.) and cucumber seeds (Hernandez-Ruiz and Arnao 2008a, b; Posmyk et al. 2009).

MEL in different organs and zones showed a pronounced distribution gradient, especially in roots. Its highest level was accumulated in the apical parts of lupine and barley roots (Hernandez-Ruiz and Arnao 2008a).

Animal studies have shown the highest concentration of MEL in the cell membrane followed by mitochondria, nucleus and cytosol (Venegas et al. 2012). Lately, it has been speculated that mitochondria and chloroplasts are the primary sites of MEL generation in plants (Tan et al. 2013).

Antioxidative role of MEL

Among many functions which MEL performs in plants, its role as an antioxidant molecule and a growth promoter is most supported by experimental evidence (Paredes et al. 2009; Park 2011).

MEL is a conservative compound widespread in plant and animal kingdoms. It is an important antioxidant which activities against a variety of toxic oxygen and nitrogen species are well documented (Tan et al. 1993; Galano et al. 2011). The intermediate products of its metabolism also have antioxidant properties (Galano et al. 2013). MEL is soluble both in water and lipids, it can act as a universal hydrophilic and hydrophobic antioxidant. This fact, together with small size of this molecule, allows it to migrate easily between the compartments of cells protecting them from excessive ROS level. MEL showed much higher antioxidant activity than vitamins C, E and K. This is may be due to better penetration into the cell compartments. Whereas vitamins are capable only of selective migration (Bonfont-Rousselot and Collin 2010). These authors suggested that the efficiency of radical scavenging by MEL was highly dependent on their production site and thereby protecting lipids and/or protein against oxidation. The synergistic effect with other antioxidants such as glutathione, ascorbic acid, polyamines, etc., is also very important (Gitto et al. 2001). MEL had positive impact on cold-induced apoptosis in a suspension culture of carrot (*Daucus carota* L.) and is positively correlated with polyamine synthesis (Lei et al. 2004). Beneficial effects of MEL may also result from its signaling function. Through the induction of different metabolic pathways, this compound is able to stimulate the production of various substances, preferably operating under stress (Tan et al. 2012a; Szafranska et al. 2012a, b).

Free radical scavenging capacity of MEL extends to its secondary, tertiary and quaternary metabolites (Harderland et al. 2009). MEL interaction with ROS is a prolonged process that involves its many derivatives. It was shown that the original MEL metabolite *N*¹-acetyl-*N*²-formyl-5-methoxykynuramine (AFMK), which was identified for the first time in water hyacinth by Tan et al. (2007a) and particularly *N*¹-acetyl-5-methoxykynuramine (AMK), possessed also high antioxidant activity (Galano et al. 2013). This process is described as the free radical scavenging cascade, which makes MEL highly effective, even at low concentrations, in protecting organisms from oxidative stress (Galano et al. 2013). Evidence supports the conclusion that plants and plant products contain isomers of this indoleamine which may be also ROS scavengers (Tan et al. 2012b; Vitalini et al. 2013). MEL reduces oxidative damage of important molecules and its antioxidant activity may manifest itself in several ways: (i) direct free radical scavenging; (ii) elevating the antioxidant enzyme activity; (iii) protecting antioxidant enzymes from oxidative damage; (iv) increasing the efficiency of the mitochondrial transport chain and (v) reducing the generation of free radicals (Tan et al. 2010).

Increased levels of MEL help plants to protect themselves against environmental stress caused by water and soil pollutants. Arnao and Hernandez-Ruiz (2013) showed more MEL accumulated in leaves, stems and roots of tomato plants cultivated in opened field conditions in comparison to that which were cultivated in chamber and in vitro culture. High MEL concentration in alpine and Mediterranean plants exposed to UV radiation as well as in tomato (*Lycopersicon esculentum* Mill.) and tobacco (*Nicotiana tabacum* L.) resistant to ozone suggests a protective role of this molecule related to its antioxidant properties. As it was also observed in tomato fruits, the concentration of MEL was much higher in mature than in green ones, which may be related to the protection of fruit against intensive production of ROS during ripening (Posmyk and Janas 2009). Interestingly, that pretreatment of callus of *Rhodiola crenulata* prior to cryopreservation protects this tissue against oxidative damage and improves its survival (Zhao et al. 2011).

Transgenic rice plants rich in MEL were more resistant to butafenacil, a herbicide which induces oxidative stress (Park et al. 2013b). Due to antioxidant properties, MEL protected the roots of barley from the damaging effects of NaCl, ZnSO₄ and H₂O₂ (Tan et al. 2010). Exogenously applied MEL protected a macroalga *Ulva* sp. against the effect of elevated temperature and high heavy metal concentrations (Tal et al. 2011). This agrees with results of by Posmyk et al. (2008) where the pre-sowing seed treatment with MEL also protected red cabbage seedlings against toxic Cu ion concentrations as well as MEL application to cucumber and corn seeds had a beneficial effect on seed germination, the growth of seedlings and crop production of plants which germinated from them, especially those subjected to cold stress (Posmyk and Janas 2009; Posmyk et al. 2009).

Animal studies using MEL indicate its effect on the fluidity of membranes protecting them from environmental stresses and keeping them in the proper consistency (Garcia et al. 1997; Venegas et al. 2012). This indoleamine influence on cell membranes could be similar in plants, but research on this topic is still limited (Szafranska et al. 2012a, b; Tan et al. 2012a).

The results from our group showed that MEL added to *Vigna radiata* L. seeds protected the roots of chilled seedlings after re-warming and that simultaneously synthesis of phenolic compounds increased (Szafranska et al. 2012a, b), particularly of derivatives of *p*-coumaric acid (data not shown). Plants having a higher content of MEL cope better with stress under adverse environmental conditions compared to those with lower levels of this compound (Zhang et al. 2012). Tan et al. (2010) suggested that the preservation of other antioxidants by MEL suggest that this compound is the first line of defense against the

oxidative stress and that other antioxidants may be used for other purposes, as back-up protection after MEL is consumed.

MEL effectively lowered chlorophyll degradation in aging leaves of barley (*Hordeum vulgare* L.) (Arnao and Hernandez-Ruiz 2009) and detached leaves of apple (*Malus domestica* Borkh. cv. Golden Delicious) protecting the photosystems from damage (Wang et al. 2012). This indoleamine also increased photosynthetic efficiency of chlorophyll in plants (Tan et al. 2012a). Exogenous MEL at 10 mM delayed also the process of dark-induced senescence in detached apple leaves possibly through regulation of the ascorbate–glutathione cycle (Wang et al. 2012).

Regulatory roles of MEL in plants

MEL in plants can regulate rhythmic physiological processes (Tal et al. 2011; Park 2011). Level of this indoleamin increases at night and decreases during the day MEL which is why it is called the hormone of darkness in animals (Reiter 1991a, b). However, light influence on MEL biosynthesis during rice leaf senescence is in contrast to animals (Byeon et al. 2012). A pattern of MEL synthesis similar as in animals was observed in many plant species although in some photosynthetic species it can be synthesized also during the day (Posmyk and Janas 2009; Tan et al. 2012a). It seems that this may be related to the antioxidant function of this indoleamine, because during photosynthesis large amounts of ROS are produced.

Exogenously applied MEL affects developmental processes during both vegetative and reproductive growth. This compound has similar chemical structure as auxin–IAA so it seems that it may play a similar role in plants as this hormone. In fact, the influence of MEL on vegetative growth was similar to that of auxin: at the low level (1 μ M) MEL caused auxinic response concerning the number and length of roots, but at the higher level (10 μ M) it inhibited rooting as in sweet cherry rootstocks (Sarropoulou et al. 2012). Serotonin, the precursor of MEL, at 10–160 μ M stimulated lateral root growth in *Arabidopsis thaliana* L. whereas at higher concentrations it inhibited primary and lateral root growth, and promoted formation of adventitious roots (Pelagio-Flores et al. 2011).

The effects of MEL may be indirect by influencing the auxin levels but during reproductive development it may act as a transition signal indicating the time for seed germination (Park 2011). Can MEL act as a hormone independently, or in concert with auxin and its own precursors and metabolites? The research on MEL and serotonin in plants is still in its infancy and little is understood of their roles in plant growth and development.

Research has shown that MEL exerts multiple effects on plant development. It seems that resumption of the research on classic plant models is necessary in order to clarify the role and mechanism of MEL action (i) as an independent plant growth regulator, (ii) as a factor mediating the activity of other substances influencing plant growth or (iii) as a substance involved in growth regulation but whose activity generally is ascribed to other compounds (Park 2011).

Can MEL be one of plant biostimulators? Its potential usage in horti- and agriculture

Research carried out during the last two decades has shown that some natural products may be efficiently used to enhance plant tolerance to biotic and abiotic stresses. Biostimulation may be the most promising method to enhance ecological crops, to protect it in environment, and to support safety-food production. A group of active products which can cause plant biostimulation is presently classified as biostimulators. Biostimulators are different kinds of non-toxic substances of natural origin that at low concentrations improve and stimulate plant life processes otherwise than fertilizers or phytohormones. Their effect in plants results from their influence on plant metabolism in a wide sense of the word. They can stimulate the synthesis of phytohormones, facilitate the uptake of nutrients from the substrate, stimulate root growth, and contribute to a higher yield and improve its quality. They are agents which increase resistance of plants to unfavorable conditions as extreme temperature, drought, heavy metals etc. (Basak 2008). Although the effects of biostimulators are not so spectacular and not always stable over the years (due to interactions with other used chemicals and/or environmental factors)—the agricultural interest in using biostimulators is increasing because they are safe for natural environment and can potentially replace pesticides.

In recent years, biologically active substances with potential uses in agriculture and horticulture have been isolated from smoke obtained from burning plant material. One of them is butenolide (3-methyl-2H-furo[2,3-c]pyran-2-one) termed karrikinolide (KAR). Treatment with smoke–water showed increased seed germination as well as seedling growth and yield of many plant species including crop plants such as tomato, bean, okra and maize. This phenomenon is more pronounced under stress conditions (Kulkarni et al. 2011).

It seems that biostimulation with use MEL may be the most promising method to enhance ecological crops, to protect the environment, and to support safety-food production. The pre-sowing seed treatment with MEL protected red cabbage seedlings against toxic Cu ion

concentrations as well as MEL application to cucumber and corn seeds had a beneficial effect on the growth of seedlings and crop production of plants which germinated from them, especially those subjected to cold (Posmyk and Janas 2009; Posmyk et al. 2009) and water-stress (Zhang et al. 2013).

Biostimulators are recommended as a preventive or an intervention method and they can be applied before expected stress, during or after stress, e.g., frost, drought, salt (Li et al. 2012).

The research carried out in Department of Ecophysiology and Plant Development at Lodz University on the influence of exogenous MEL on plant growth showed that this compound promoted not only seed germination (Posmyk et al. 2009; Posmyk and Janas 2009) but also plant development and yield. The preliminary experiments which were conducted in the years 2009 and 2011 in the open field conditions showed that plants from seeds of corn (*Zea mays* L.), mung bean (*Vigna radiata* L.) and cucumber (*Cucumis sativus* L.), hydroprimed or osmoprimed with

MEL had higher crop yield than the control ones (Figs. 1, 2, 3). 50 and 500 μM MEL-treated corn plants had more and larger cobs than those hydroprimed without MEL and the non-primed plants (Fig. 1). Similar results we observed with mung bean whose seeds were hydroprimed with MEL at 20, 50 and 500 μM concentrations. The number of pods was greater in plants grown from the seeds hydroprimed with 50 μM MEL than in hydroprimed without MEL and non-primed ones. It seems that 500 μM MEL concentration used in seed priming was too high, and the number of pods was fewer in comparison to the seeds hydroprimed without MEL and non-treated ones (Fig. 2). At harvesting, 50 μM MEL osmoprimed cucumber plants had more fruits than those osmoprimed with MEL 500 μM , osmoprimed without MEL or non-treated plants. We observed that some fruits of MEL-treated plants were larger than those osmoprimed without MEL and non-osmoprimed ones (Fig. 3). It is surprising that the one-time MEL application to the seeds gave a significantly positive effect on the yield of plants which grew naturally in the field. It was assessed that the



Fig. 1 Effect of melatonin pre-sowing treatment on corn (*Zea mays* L.) yield. Corn seeds were hydroprimed with MEL at different concentrations (HMEL50, HMEL500). Seeds hydroprimed with water (H) and non-primed (N-P) were established as the control. Plants were

grown in the field, under natural conditions, without further treatment. The presented yield originated from the same number of plants in each experimental variant. The experiments were conducted in 2009



Fig. 2 Effect of melatonin pre-sowing treatment on mung bean (*Vigna radiata* L.) yield. Mung bean seeds were hydroprimed with MEL at different concentrations (HMEL20, HMEL50, HMEL200). Seeds hydroprimed with water (H) and non-primed (N-P) were

established as the control. Plants were grown in the field, in natural conditions, without further treatment. Presented yield originated from the same number of plants in each experimental variant. The experiments were conducted in 2011



Fig. 3 Effect of melatonin pre-sowing treatment on cucumber (*Cucumis sativus* L.) yield. Cucumber seeds were osmoprimed with MEL at different concentrations (OMEL50, OMEL500). Seeds osmoprimed with water (O) and non-primed (N-P) were established

production of corn, cucumber and mung bean primed with MEL was about 10–25 % greater in comparison to those primed without MEL and it depended on plant species. To explain this phenomenon, proteomes isolated from the control and MEL-primed seeds are currently being analyzed in our department. We are aiming to get information which of the proteins and metabolic pathways are modified by MEL applied to seeds.

Tan et al. 2007a investigated the potential relationships between MEL supplementation and environmental tolerance of plants. Their results showed that applying MEL to the roots of *Malus hupehensis* Rehd. seedlings prior to salinity treatment partially alleviated the salt-induced inhibition of plant growth, and slowed down the decrease in photosynthesis rates and chlorophyll content (Li et al. 2012).

In summary it can be speculated that MEL is safe to animals and humans (Bonfont-Rousselot and Collin 2010) as well as inexpensive, this may be a feasible and cost-effective approach to remove environmental contaminations. Further research in this area could provide valuable information on the significance of plant-derived dietary supplements, agriculture and environment phytoremediation, however the present knowledge justifies the belief that MEL could be used as an effective biostimulator in agriculture and can improve crop production in changing environment.

Conclusions

The goal of this review is to update the reader on the various interactions of MEL and to encourage plant scientists to further investigate this potentially useful molecule. This area could prove useful in solving numerous questions regarding the role of MEL in plants and its possible practical application to ecological agriculture.

Using MEL as a biostimulator, we can increase its content in plant but it is worth noting that oral administration of MEL (dosages from 1 to 300 mg) as well as even 1 g MEL daily for 30 days resulted in no negative side

as the control. Plants were grown in the field, in natural conditions, without further treatment. Presented yield originated from the same number of plants in each experimental variant. The experiments were conducted in 2011

effects (Bonfont-Rousselot and Collin 2010). Thus, it can be suggested that higher level of MEL in plant foods may be beneficial to animals/humans consuming them. Exogenous application of this substance increasing its content above the physiological level can enhance quality of life in advanced age as well as protect an organism against cancer and cardiovascular disease (Fernandez-Mar et al. 2012).

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