Role of Melatonin in Maintaining Post Harvest Quality of Fruits: A Review

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Abstract
Melatonin (N-acetyl-5-methoxytryptamine) is a nontoxic biodegradable molecule produced naturally in a pineal gland of animals and different tissues of plants. It is an indispensable signaling molecule, involved in plethora of biochemical mechanism in plants. Melatonin can be used as eco-friendly safe substance for maintaining plant growth and development and can be used for the promotion of organic farming. Production of melatonin endogenously in different organs of the plant has played magnificent role in alleviating several environmental stresses by regulating ROS and RNS, delayed chlorophyll degradation, enhancing photosynthesis, triggering plant hormones, accelerating different antioxidant enzymes and modulating gene expression in plants. However, to counteract unfavorable environmental factors, melatonin produced by the body is occasionally insufficient. In order to sustain plant immunity and growth capabilities, exogenous melatonin and other techniques needs to be implemented as exogenous application of melatonin addresses the major postharvest-related issues such as chilling injury and fruit decay. It also delays senescence in various horticultural crops, and thereby helps in extending the shelf life without adversely affecting nutritional quality. In this review, the role of endogenous and exogenous melatonin on various fruits was studied.

Keywords: Melatonin, shelf life, nutritional quality, eco-friendly

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Introduction
Melatonin (N-acetyl-5-methoxytryptamine) is a non-toxic signalling molecule ubiquitously found in different plant species [1]. It was discovered in the bovine pineal gland in the year 1958 by Arnon Lerner [2]. Melatonin is an important pleotropic molecule and has tryptophan as its precursor whereas its intermediate is said to be serotonin (5-hydroxytryptamine), also called as indoleamine [3]. Its presence in numerous living systems, ranging from the simplest microorganisms like bacteria to the most sophisticated ones like humans, animals and plants has been recognized and investigated. Improvements in seed germination, photosynthesis, biomass production, circadian rhythm, redox network, membrane integrity, root growth, leaf senescence, osmoregulation, and abiotic stress have all been linked to melatonin [4]. As a safe and nontoxic chemical, melatonin has shown promise in the transportation and storage of horticultural crops. Additionally, it has been shown to be advantageous in terms of ensuring the highest possible agricultural productivity and food safety while yet being environmentally benign. Exogenous melatonin administration has been shown to slow the postharvest ripening of various horticultural crops, including peach [5], pear [6], grape [7], bananas [10, 11], apples [7], guava fruit [8], and pomegranate [9]. Its significance or application in postharvest management of fruits or vegetables is yet in its infancy, despite substantial study on its role in plants in response to biotic and abiotic stresses including salt, drought, and various fungal/bacterial infections. [12]

Reactive oxygen species (ROS), which act as a ripening stimulant by oxidizing proteins and membrane lipids, are often linked to the generation and emission of fruit ripening [13]. During fruit ripening, melatonin administration can increase endogenous melatonin levels, which can affect the quality and shelf life of fruits like pears [14] and bananas [10]. The application of melatonin can promote enzymatic and non-enzymatic antioxidant properties to scavenge ROS, which in turn helps in delaying fruit ripening and maintaining the quality of fruit [15].

Melatonin is an innovative bio stimulator that has a variety of uses in postharvest physiology and other aspects of plant growth and development. Melatonin has been reported to be linked to a number of plant stresses, Salinity stress [16], drought stress [17], and nutritional deficiency [18]. Awareness of consumers all around the world are increasing regarding the safety and the quality of food with higher nutrient content, and the use of natural preservative as
alternatives of synthetic chemicals for production of horticultural crops, which have beneficial impact on human health [19]. In this sense, the use of natural bio-stimulator like melatonin for increasing the production of horticultural crops has paid much consideration to the researchers.

**Biosynthesis of melatonin**

Melatonin is derived from tryptophan which is synthesized in fruit tissues which include seeds, peel, and pulp. Melatonin biosynthesis begins with tryptophan. It involves four enzymatic steps and six enzymes. Four enzymes identified in different fruits are tryptophan, tryptamine, serotonin, N-acetylserotonin, and 5-methoxytryptamine [20]. The genes encoding these enzymes are identified as Tryptophan decarboxylase, tryptophan hydroxylase, tryptamine 5-hydroxylase, serotonin N-acetyltransferase, N-acetylserotonin methyl transferase [21]. The enzyme tryptophan decarboxylase catalyzes tryptophan into tryptamine. Tryptamine is then converted into serotonin (5-hydroxytryptamine) by 5-hydroxylase tryptamine, serotonin is an essential intermediate for melatonin synthesis in the plants. In the third phase, serotonin is converted to N-acetyl serotonin by N-acetyl transferase and in final phase to melatonin with the help of N-acetyl serotonin methyl transferase [22]. Recent research has suggested that there may be several mechanisms for melatonin production, and there is disagreement about how best to predict how serotonin will be converted to melatonin. Serotonin is first acetylated and then O-methylated to generate melatonin in the first process (NM route), but in the second process, serotonin is first O-methylated and then acetylated to form melatonin (MN pathway).

**Site for melatonin biosynthesis**

Based on research by various researchers the melatonin biosynthesis occurs mainly in the chloroplast and mitochondria of the plant cells. It was reported that N-acetyl serotonin is synthesized in chloroplast of the plant cells and subsequently transported to cytoplasm for O-methylation to form melatonin (NM pathway) which is prominent melatonin biosynthetic pathway in plants [23].

**Methods for detection for melatonin in fruits**

Melatonin in fruits is detected using various methods such has GC (gas chromatography), HPLC (high performance liquid chromatography), UPLC (ultrahigh performance liquid chromatography), HPLC-ECD (high-performance liquid chromatography with electrochemical detection [24], ELISA (enzyme-linked immunosorbent assay). HPLC and UPLC are most commonly used for melatonin detection in different fruits such as citrus [25], grape [20], mulberry [26], and apple [27]. GC is rarely used. Generally, C18 SPE cartridge used before HPLC and UPLC increases melatonin content detection. Different extraction solvents are used for each method which may include methanol, acetone-methanol, perchloric acid, and sodium carbonate and ether. Melatonin was measured and it was reported that several factors such as type of solvent, volume of solvent, temperature, sonication time and pH influenced melatonin extraction efficacy and it was found that methanol was the best solvent when it was extracted at the temperature range of 25–30 °C with a pH of 7.6 and 20-min. [28]

**Presence of endogenous melatonin in fruits**

Given the several functions of melatonin in humans, study was done on plants. Its presence in plants was first discovered in 1995, as a result significant research was done on its presence and melatonin has been found to be widely distributed in a variety of plants, including herb, vegetable, and fruit plants [29] and in a wide range of plant organs, including roots, stems, leaves, flowers, fruits, and seeds, which contained 15–100 times more melatonin than was often found in other plants [30]. Because of these significant differences in endogenous melatonin levels between different plant species, it was hypothesised that melatonin function differed from plant to plant. Numerous studies have established the existence of endogenous melatonin and its variation among various horticultural crops as well as various fruit varieties, including, tomato and strawberry [31], banana [32].

**Concentration of melatonin in plants**

Melatonin levels in plants fluctuate over time within the same plant, reaching their highest levels during times of stress. Due to increased activity of serotonin N-acetyl transferase and N-acetyl serotonin methyl transferase, melatonin synthesis in rice seedlings (in vivo) was boosted at higher temperature and dark circumstances. Similar to
this, it differs across individual plants and within-species variations cultivated under diverse agro-ecological circumstances [33].

In two cultivars, such as "Hongdeng" and "Rainier," it was assessed that the melatonin synthesis in sweet cherry changes in its concentrations over a period of 24 hours throughout development and ripening. It was claimed that melatonin production was induced in both of these types by both darkness and oxidative stress. In addition, exposure to high light intensities and high temperatures were linked to increased melatonin production. Results showed that the tryptophan decarboxylase enzyme decreased the synthesis of melatonin by examining the plant tryptophan decarboxylase gene (PaTDC) in cherry [34].

### Role of melatonin in post-harvest fruits

As much as 20–40% of postharvest losses in perishable goods like fruits and vegetables occur during various postharvest handling stages, including harvesting, shipping, storage, and marketing. Therefore, when managing fresh produce, including correct pre-cooling, sorting, and grading, packaging, and storage, effective and efficient postharvest management procedures are essential. Several post-harvest procedures have been suggested for easing chilling damage, minimising decay, and slowing the ripening process, all of which improved the produce's shelf life. In recent years, several compounds have demonstrated their promise for use in the postharvest management of various fruits and vegetables, including 1-methylcyclopropene (1-MCP), nitric oxide (NO), salicylic acid (SA), and brassinosteroids (BRs). A review of current literature found that melatonin can replace these substances and/or methods because it has demonstrated a possible role in the postharvest management of fruits.

In humans, animals, and higher plants, melatonin's remarkable antioxidant effects have been demonstrated both in vivo and in vitro. In addition to removing reactive oxygen species (ROS) from plants, melatonin also stimulates the production of antioxidant enzyme genes. Additionally, melatonin can control several physiological metabolisms in higher plants as a signal molecule [35].

![Melatonin]

**Figure 1** Representation of melatonin’s role in maintaining quality of postharvest fruits

### Role of melatonin in control of decay

The majority of fruits have a very high moisture content and are therefore extremely susceptible to microbial infection, which leads to rotting in the harvested produce. Therefore, it’s critical to shield them against microbial deterioration, physical harm, and mechanical damage. Melatonin, a strong antioxidant, has demonstrated its ability to prevent deterioration by inhibiting the growth of certain fungi, bacteria, and other microorganisms. Research investigated the efficiency of exogenous melatonin application against fungi, specifically the green mould of citrus, and discovered that it reduced the disease by scavenging defense-related ROS in the afflicted fruits. Melatonin's preventive function against plant fungal infections has been explained by a number of different theories. For instance, some researchers have suggested that melatonin's defense mechanism involves its capacity to keep hydrogen peroxide levels in cells at a safe level as well as the production and control of antioxidant enzyme (superoxide dismutase, ascorbate peroxidase) activities [36]. The underlying mechanism of gene regulation is not entirely understood, even if exogenous melatonin activates the genes that code for antioxidant enzymes. Therefore, fascinating research should be encouraged to unravel the mechanisms.

There are a number of methods that are popular worldwide to prevent decay in harvested product, but lately melatonin has also been reported to prevent it in some fruits. For instance, the advantageous effects of melatonin...
therapy on reducing postharvest degradation in the stored strawberry fruits, which have been associated with increased GABA-T (Gamma aminobutyric acid-transaminase) enzyme activity. In addition, strawberry fruits accumulated hydrogen peroxide in response to melatonin treatment, which activated the phenyl propanoid pathway and caused hydrogen peroxide to accumulate. This was caused by higher SOD (superoxide dismutase) enzyme activity concurrent with lower CAT (catalase) and APX (ascorbate peroxidase) and APX enzyme activity [37].

In addition, due to melatonin’s probable function in regulating pathogenic fungal infection, the Botrytis rot in apples was successfully suppressed by exogenous melatonin application [38]. The melatonin supplementation increased the antibacterial activity and reduced browning in apple juices. Additionally, plums kept in cold storage that had been treated with melatonin (1,000 M) displayed a larger decline in the incidence of decay than those that hadn't been [39]. Similar to this, exogenous melatonin administration prevented Botrytis rot in tomato, and pears [40] by stimulating the jasmonic acid signalling system against botrytis rot.

**Role of melatonin in control of chilling injury**

Exogenous melatonin therapy has been demonstrated in recent years to increase chilling tolerance and lessen chilling injury in postharvest fruit during cold storage, including peach [5], tomato [41], pomegranate [42], and sapota [43]. In postharvest fruits stored at low temperatures, exogenous melatonin therapy decreased the amount of malondialdehyde (MDA), electrolyte leakage, and lipoxygenase (LOX) activity. But following several melatonin treatments, the firmness of the fruit changes in a different way.

For instance, a lengthy treatment lasting 120 minutes considerably lowered the firmness of peach fruit while a 10-minute 0.1 mM melatonin treatment dramatically increased it [5]. The prevalence of chilling injury in postharvest fruit is also significantly influenced by ROS. Exogenous melatonin treatment significantly increased non-enzymatic and enzymatic antioxidants, including SOD, CAT, APX, POD, GR, phenols, and AsA, that scavenge ROS of postharvest fruit during low temperature storage [39].

Exogenous melatonin therapy can block PPO activity and lessen fruit oxidation [43]. Furthermore, it should be highlighted that exogenous melatonin therapy increased the levels of endogenous melatonin and NO in postharvest fruit during cold storage, scavenging the generation of ROS. It was also conferred that the induced chilling tolerance in tomato fruit melatonin treatment might be attributed to the triggered arginine pathway leading to the accumulation of endogenous polyamines, proline [44].

**Role of melatonin in control of fruit ripening**

Unpalatable fruits become pleasant through the complex physiological and biochemical process of fruit ripening. According to Sharma [45], the primary physiological and biochemical changes related to fruit ripening include tissue softening, peel colour change, increased respiration and ethylene evolution rates, sugar metabolism, and organic acid metabolism. For instance, ethylene controls the ripening of tomatoes, which results in changes such as the production of carotenoids and lycopene, the conversion of starch to sugars, and an increase in the activity of enzymes that break down the cell wall. Exogenous melatonin application promoted postharvest ripening of tomato fruits by positively controlling ethylene production and signaling, which resulted in changes in biochemical processes like lycopene and carotenoid accumulation, cell wall degradation, and volatiles biosynthesis [46]. The mechanism of melatonin in the "Moldova" grape berries in controlling fruit ripening was explored and they found that melatonin at a concentration of 100 M effectively enhanced the levels of ABA, H2O2 and ethylene production and promoted berry ripening [47].

Pomegranates [43], jujubes [48], both have higher phenolic content and antioxidant activity. Improvements were made in the concentration of cyanin-3-O-glucoside, peonidin derivatives, two grape flavanols, and their derivatives. Exogenous melatonin's impact on the production of aromatic volatiles in pears was clarified [40], and its beneficial impact on the synthesis of C6 aromatic substances was determined. Even though melatonin's various actions vary, its fundamental function was to regulate the expression of the genes that code for LOX, HPL, and AAT. The postharvest quality and longevity of strawberries, peaches, grapes, have all benefited from melatonin therapy [37, 21, 48].

In addition to increasing the activity of antioxidant enzymes including SOD, CAT, and APX, melatonin administration also boosted the antioxidant content of AsA and GSH, which in turn decreased the production of oxygen radical [49]. Similarly exogenous melatonin significantly reduced membrane leakage by decreasing the formation of superoxide and peroxide radicals, which in turn delayed discoloration and pericarp browning in some litchi fruits.

**Role of melatonin in delay of senescence**

In contrast to fruit ripening, senescence causes a steady decline in fruit quality. Fruit gradually loses its capacity to
regulate its internal environment and react to its storage environment as it ages, and its tissue structure and nutritional elements also deteriorate [50]. Exogenous melatonin therapy has been shown to dramatically slow down postharvest senescence during storage, extending shelf life. Melatonin treatment preserved fruit firmness by delaying cell wall deterioration [49], decreasing weight loss and respiratory rate [7], maintaining levels of TSS and soluble sugars [49], inhibited peel browning etc.

It is believed that ROS are essential for fruit senescence during postharvest storage. Biological macromolecules found inside of cells, such as nucleic acids, lipids, and proteins, can sustain oxidative damage from ROS [50]. Fruit have developed effective enzymatic and non-enzymatic antioxidant mechanisms to scavenge ROS and prevent oxidative damage. It’s interesting to note that in the beginning of storage, the ROS content in the melatonin-treated tomato fruit considerably rose [51]. As a result, it was hypothesized that a brief increase in postharvest fruit ROS during the initial stages of storage might help to activate the enzymatic and non-enzymatic antioxidative systems, which would then help to slow down senescence and boost overall resistance to environmental stress during storage.

Fruit senescence after harvest may be influenced by other signaling molecules and plant hormones connected to melatonin. It has been shown that postharvest fruit treated with exogenous melatonin produced significantly more NO and had endogenous melatonin levels that were higher [52]. In addition to preventing the generation of ROS, melatonin and NO treatments also prevent the ethylene synthesis in the postharvest fruits. Hence, exogenous melatonin treatment might play important roles in delaying senescence of postharvest fruit.

Conclusions

In terms of reviewed literature, the melatonin has its beneficial role in upregulation of defense genes, antioxidant enzymes such as SOD, POD, Polyamines, and CAT. It helps in regulation of endogenous levels of NO, ROS and different plant hormones to affect various metabolisms being an efficient signalling molecule and maintain quality of postharvest fruits. Using exogenous melatonin, the oxidative damage, degradation of cell wall, ethylene synthesis and release of aroma are delayed in the post-harvest fruits. Melatonin via cross-linking with the various hormones such as GABA, JA, NO, IAA, ABA, ethylene and SA helps in controlling decay, chilling injury, ripening and delaying, senescence and extending the shelf life of the postharvest fruit. Being a natural bio-stimulator, use of melatonin can be encouraged for improving the post-harvest quality of a variety of plants and vegetables. Although studies have shown that melatonin can be used to control plants after harvest, the specific mechanism by which it works and how it works are still unknown. Since the regulating system is still in its infancy, more research should be done to understand it. Being a non-toxic, biodegradable chemical, melatonin could be used to support organic farming. Hence melatonin has a diverse role in post harvest management for maintaining quality of fruits.

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