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Review

Melatonin in grapes and grape-related foodstuffs: A review

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ABSTRACT

A decade has passed since melatonin was first reported in grapes in 2006. During this time, melatonin has not only been found in the berries of most wine grape (*Vitis vinifera* L.) cultivars, but also in most grape-related foodstuffs, e.g. wine, grape juice and grape vinegar. In this review, we discuss the melatonin content in grapes and grape-related foodstuffs (especially wine) from previous studies, the physiological function of melatonin in grapes, and the factors contributing to the production of melatonin in grapes and wines. In addition, we identify future research needed to clarify the mechanisms of grape melatonin biosynthesis and regulation, and establish more accurate analysis methods for melatonin in grapes and wines.

Contents

1. Introduction

Vitis is widely cultivated around the world. According to the OIV statistical report on world vitiviniculture (OIV., 2016), global grape planting areas have increased rapidly in recent years, and are forecast to reach 7.53 Mha in 2015. As an important grape product, wine is an alcoholic beverage that is enjoyed globally. In 2015, global wine production and consumption reached 27.44 and 24 GL, respectively. The prevalence and distribution of grapes and wines in the world is not only due to their unique sensory characteristics, but also to their high nutritional value and health-promoting properties. Melatonin, which was recently reported to be present in wine in 2008, as well as resveratrol and hydroxytyrosol, are

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regarded as bioactive compounds in grapes and wines (Fernández-Mar, Mateos, García-Parrilla, Puertas, & Cantos-Villar, 2012; Iriti & Faoro, 2006; Iriti & Faoro, 2009; Iriti & Varoni, 2016) that have positive effects for human health.

Melatonin (*N*-acetyl-5-methoxytryptamine), which has a low molecular weight and an indole-based structure, is ubiquitous in living organisms. Melatonin was originally isolated and identified in the pineal gland of cows (Lerner, Case, & Takahashi, 1958). For a long time thereafter, melatonin was considered exclusively as an animal hormone, specifically a neurohormone (Reiter, 1991). During this period, with very few exceptions, all research related to melatonin was performed in either animals or the tissues and cells of animals. Since the first report of melatonin in plants in 1995, melatonin has been identified in many different plants in a wide range of concentrations (from picograms to micrograms per gram of tissue) (Tan et al., 2012). Currently, its physiological function, biosynthesis pathway, physiological and molecular regulation mechanisms, have become areas of research interest in the field of botany. In 2006, it was first reported that melatonin exists in grapes (Iriti, Rossoni, & Faoro, 2006). Thereafter, there has been continued research on grape and wine chemistry, with a focus on melatonin. After a decade of development, considerable research progress has been made on melatonin in grapes and wines, similar to the progress made on melatonin in other plants. Therefore, it is necessary to periodically review this research and establish expectations for future studies.

Previously, Iriti and Varoni (2016) reviewed melatonin in grapes and wines from the perspective of human health promotion. In our review, we focus on the content of melatonin and its isomers in grapes and wines, the factors causing changes in melatonin content, melatonin biosynthesis in grapes, and the physiological function of melatonin in grapes.

2. Melatonin in grapes

2.1. Melatonin content in grapes

Table 1 summarizes the melatonin contents in grape berries reported in previous studies. In 2006, melatonin was first detected in the berry skin of eight different *Vitis vinifera* cultivars (Nebbiolo, Croatina, Sangiovese, Merlot, Marzemino, Cabernet Franc, Cabernet Sauvignon and Barbera) cultivated in Treviso, Italy, with levels ranging from 0.005 to 0.965 ng/g (Iriti et al., 2006). Stege, Sombra, Messina, Martinez, and Silva (2010) obtained similar results (0.6–1.2 ng/g) for the same tissue of Malbec, Cabernet Sauvignon and Chardonnay cultivars in Argentina. Much higher melatonin concentrations (9.3–17.5 ng/g) were found in the berry skin of Malbec cultivars in Argentina (Vitalini, Gardana, Zanzotto, Simonetti, et al., 2011b), whereas the melatonin contents in the seeds and flesh ranged from 3.5 to 10 ng/g and from 0.2 to 3.9 ng/g, respectively, during the transition from pre-veraison to veraison of Merlot cultivars. Much higher melatonin concentrations were observed in whole berries (100–150 μg/g), depending on the phenological stage, for Merlot cultivars grown in Canada (Murch, Hall, Le, & Saxena, 2010), while only 1.2 and 1.5 ng/g of melatonin were observed in Sangiovese and Albana grapes, respectively (Mercolini, Mandrioli, & Raggi, 2012). However, overall, most studies reveal that the melatonin content in grapes is on the order of ng/g.

2.2. Factors impacting melatonin content in grapes

The differences in reported melatonin levels can, in part, be explained by many endogenous and external factors, such as the genetic traits of the cultivar, the berry tissue/grapevine organ analysed, the phenological stage, pathogen infections and phytosanitary treatments, agro-meteorological conditions and environmental stresses, and the vintage.

The melatonin contents in the different tissues of a grape berry change with the phenological stage. A study by Vitalini et al. (2011b) showed two different trends: the highest melatonin content was observed in the skin during pre-veraison, which then decreased by 47% during veraison; whereas, the transition from pre-veraison to veraison increased the melatonin content by 63% in the seed and by 95% in the flesh. Moreover, during veraison, the melatonin concentration in the seed was significantly higher than that measured in the skin and flesh. In whole berries, the concentration of melatonin was highest in wine grapes harvested during the early stages of veraison when the seed is developing (Murch et al., 2010). The relative concentrations of melatonin in the various berry tissues were somewhat different from those of total polyphenols and anthocyanins, which accumulate significantly during grape berry ripening (Conde et al., 2007).

Melatonin levels also fluctuate during the day/night cycle in the fruit organs of *Vitis vinifera* grown under field conditions (Boccalandro, González, Wunderlin, & Silva, 2011). To further confirm these results, Boccalandro et al. (2011) determined that the diurnal decay of melatonin in berry skins is induced by sunlight, as covered grape bunches retained higher melatonin levels than exposed ones. Therefore, light exposure may influence the amounts of melatonin detected. Herein, procedures for extracting melatonin from grape berries were usually carried out under dim green light to prevent analyte degradation.

Some chemical inducers can also modify the melatonin levels in grape berries. Field treatments of grapevines with the plant defence activator benzothiadiazole greatly increased the melatonin content in berry skin extracts, indicating a possible strategy for raising the content of this important pharmaconutrient in plants, while inducing resistance to pathogens (Vitalini, Gardana, Zanzotto, Fico, et al., 2011a).

Finally, sample preparation and determination methods are also an important factor. The extraction conditions, analytical method, type of chromatographic column and elution conditions, could impact the accuracy of the result. Based on this, we summarized the conditions used in all studies to date on melatonin content in grapes (Table 1), and found that none of the methods used in these papers were completely the same. Meanwhile, few studies compare the melatonin content in grapes obtained using different extraction and analytical methods. However, a study on the melatonin content of wine clearly showed that the contents obtained using HPLC-MS/MS were dozens of times higher than those obtained using ELISA for eight monovarietal wines (Rodriguez-Naranjo, Gil-Izquierdo, Troncoso, Cantos, & Garcia-Parrilla, 2011). In addition, the amphipathic nature of melatonin and the chemical complexity of plant extracts can also cause variation in melatonin quantification (Gomez, Hernández, Martinez, Silva, & Cerutti, 2013). Byeon and Back (2014) re-examined melatonin concentrations in rice plants using various extraction methods and found that the obtained levels varied depending on the extraction conditions. The melatonin levels in rice tissues after 50% methanol extraction were undetectable, whereas chloroform extraction yielded melatonin levels of 0.69 ng/g fresh weight. In contrast, a modified method using chloroform/methanol (30:1) yielded melatonin levels of 1.65 ng/g fresh weight, which is 2.4 times higher than that obtained using chloroform extraction. According to the existing experimental data, chloroform/methanol (30:1) or methanol/water/formic acid (80:20:1) extraction combined with UPLC-MS/MS technology is the optimal analytical method for analysing melatonin levels in grape berries. However, it is crucial to develop more accurate analysis and detection methods in future studies.