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The good health of Bacchus: Melatonin in grapes, the unveiled myth

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A B S T R A C T

The first detection of melatonin in grapes appeared in 2006 with the questioning title 'Melatonin content in grape: myth or panacea?'. Then, in a Letter to the Editor of Journal of Pineal Research, the lead journal covering all aspects of physiology, pathophysiology and endocrinology of melatonin in vertebrates (and all other species), dated 2009, panacea triumphed on myth (the title was 'Melatonin in grape, not just a myth, maybe a panacea') (Iriti, 2009). This meant that, despite the preliminary and incomplete reports regarding melatonin in grapes, a new *tessera* was added to the mosaic of the complex grape chemistry, further substantiating the health potential of grape products. Since then, melatonin and its isomers were detected both in red and white wines, and a number of exciting papers elucidated that both endogenous and exogenous factors may influence the biosynthesis and accumulation of these indoleamines in grapevine tissues and organs, namely varietal differences, phenological stages, day–night cycle and agrochemical treatments. Probably and similar to polyphenols and other secondary metabolites, many other environmental parameters may regulate melatonin production in grapevine, including climatic conditions, plant–microbe interactions and agricultural practices. On the other hand, because of the paucity of data on the physiological and pathophysiological roles of melatonin in grapevine, we can only hypothesize: from studies on other plants, we predict melatonin is involved in protection from oxidative and abiotic stresses.

1. Introduction

Even if melatonin (*N*-acetyl-5-methoxytryptamine) was first discovered in animal organisms, its emergence in the plant kingdom is much more ancient and, therefore, this indoleamine can properly be considered a phytochemical in evolutionary terms (Tan et al., 2010). Since the first report of melatonin in grapes (Iriti, Varoni, & Vitalini, 2010), a number of excellent papers expanded the knowledge on the levels and (patho)physiological role(s) of this molecule in grapevine (*Vitis vinifera* L.). Soon after, emphasis was paid to grape chemistry, which was enriched because of the discovery of this new bioactive component.

Among grape secondary metabolites, phenylpropanoids and isoprenoids are the most relevant (Fig. 1). Phenylpropanoids are phenylalanine derivatives including simple phenols or phenolic acids (hydroxybenzoates and hydroxycinnamates) and polyphenols (flavonoids, stilbenes and proanthocyanidines), whereas isoprenoids consist of many classes of compounds arising from acetyl Co-A: hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, triterpenes, tetraterpenes and polyterpenes (Fig. 1). As secondary metabolites, they have a plethora of functions in grapevine chemoecology. For instance, anthocyanins, a group of flavonoids, are red pigments responsible for the colour of the berry exocarp. Other flavonoids and stilbenes are phytoalexins, i.e. antimicrobial compounds, and, among stilbenes, resveratrol protects berry tissues from harmful UV radiation. For phytophagous species, proanthocyanidines, or condensed tannins, are feeding deterrents which confer astringency to unripe fruits (Iriti & Faoro, 2009a). Two classes of isoprenoids, monoterpenes and sesquiterpenes, both hydrocarbons and oxygenated derivatives, greatly contribute to the scent of flowers and fruits, attracting pronubi or repelling noxious phytophagous animals (Iriti & Faoro, 2009a). From grapes to wine, aromatic, chromatic and other quality traits of the most important Mediterranean alcoholic beverage strictly depend on grape chemicals. Phytosterols (β-sitosterol, stigmasterol and campesterol) were also recently reported in grapes (Fig. 1) (Ruggiero, Vitalini, Burlini, Bernasconi, & Iriti, 2013).

In this heterogeneous and complex scenario, which role does

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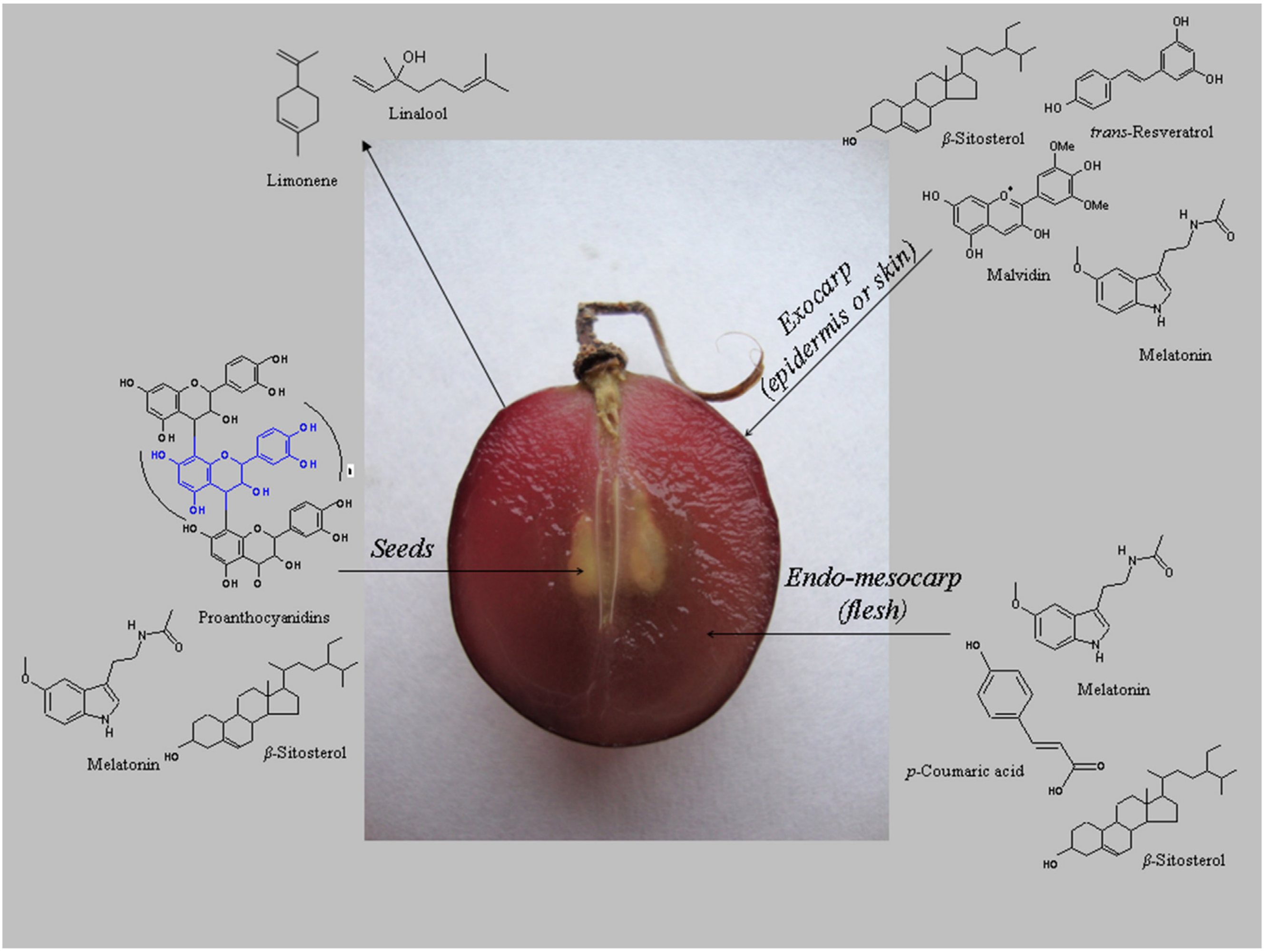

Fig. 1. Occurrence of main polyphenols (malvidin – an anthocyanins, *trans*-resveratrol and proanthocyanidins), hydroxycinnamates (*p*-coumaric acid) and new phytochemicals (melatonin and β-sitosterol – a phytosterol) in grape berry and seed tissues.

melatonin cover? We will try to answer this question, focussing on grape melatonin and briefly discussing the perspectives on human health.

2. Melatonin in grapes

The issue of melatonin in grape products began less than a decade ago, when it was detected, for the first time, in berry exocarp of Italian and France varieties (Nebbiolo, Croatina, Barbera, Sangiovese, Marzemino, Cabernet Sauvignon, Merlot and Cabernet Franc) grown in north-western Italy. Melatonin was confirmed by HPLC with fluorimetric detection, ELISA test and chemiluminescence determination. The highest levels were measured in Nebbiolo and Croatina varieties (0.96 ng/g and 0.87 ng/g, respectively), while Marzemino and Cabernet Franc showed the lowest concentrations (0.03 ng/g and 0.005 ng/g, respectively) (Table 1). Interestingly, open-field treatments of grapevine with the plant defence activator benzothiadiazole (BTH) raised the melatonin content in berry skin, thus suggesting that it may behave as a phytoalexin possibly involved in systemic acquired resistance (SAR) (Iriti, Rossoni, & Faoro, 2006).

Similar results were reported by capillary electrochromatography in the same tissue of Malbec, Cabernet Sauvignon and Chardonnay varieties (0.6 ng/g, 1.2 ng/g and 0.8 ng/g, respectively) (Table 1) cultivated in Argentina, indicating that no difference seems to exist between red and white grapes (Stege, Sombra, Messina, Martinez, & Silva, 2010).

In the whole berry (i.e. skin, flesh and seeds analysed together) of Merlot cultivar grown in Canada, much higher melatonin concentrations were measured by mass spectrometry, depending on the phenological stage. The concentration of melatonin was higher in samples collected at the green stage (pre*véraison*, around 150 μg/g) than in grapes harvested in pre-lag, transition and purple developmental stages (around 100 μg/g) (Table 1). However, the highest distribution of melatonin in vineyard occurred during the purple phase (*véraison*), when it was detected in 45% of collected samples. In contrast, the melatonin precursor serotonin was not found in any of the pre-lag phase grapes, but it was present in samples collected during the other development stages at levels of about 8–10 (Murch, Hall, Le, & Saxena, 2010).

In Merlot berry skin, we found 17.5 ng/g and 9.3 ng/g of melatonin at pre*véraison* and *véraison*, respectively (Table 1), whereas an opposite trend was observed in the other berry tissues: i.e. the transition from pre*véraison* to *véraison* raised the melatonin content both in seed (from 3.5 to 10 ng/g) and flesh (from 0.2 to 3.9 ng/g) (Table 1). Differently from melatonin, polyphenols increased from pre*véraison* and *véraison*, in skin, while decreasing in seed and flesh. Interestingly, the highest antiradical activity, determined by both DPPH (2,2-diphenyl-1-picryl hydrazyl) and ABTS [(2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)] radical-scavenging