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Comparison of the Anthocyanin Composition during Ripening of Syrah Grapes Grown Using Organic or Conventional Agricultural Practices

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The anthocyanin composition of Syrah grapes harvested at different stages of ripening and produced using organic or conventional agriculture was studied. Samples of grapes were collected from veraison to full maturity in each plot, and the content in nine anthocyanins was determined by high-performance liquid chromatography with diode array detection. The total content in anthocyanins during ripening of the conventionally grown grapes was significantly higher compared to that found in the organic production. The accumulation of anthocyanins reached a maximum 28 days after veraison (in agreement with high temperature) and then decreased until harvest. In all samples, grapes from the conventional agriculture presented higher proportions of delphinidin, petunidin, malvidin, and acylated malvidin glucosides compared to grapes from organic agriculture. In contrast with other comparative studies of organically and conventionally grown plants, the results demonstrated a higher content in anthocyanins in conventionally grown grapes.

KEYWORDS: Anthocyanins; grapes; HPLC; conventional agriculture; organic agriculture

INTRODUCTION

Anthocyanins are naturally occurring polyphenols that impart red to blue colors to fruits, vegetables, and plants (*1*). Among edible plants, red and black grapes, and the corresponding wines, constitute one of the important sources of anthocyanins. Anthocyanins are accumulated in grape skins, and this process begins after the phenological stage known as veraison. When grapes are harvested, the content in anthocyanins may be as high as 1 g/kg of grapes (*2*). The amount and composition of anthocyanins in the red grapes vary with the variety (*3*, *4*), maturity, climate (*5*), terroir (*6*, *7*), and fruit yield (*8*). In addition to their direct role in red wine color, anthocyanins also contribute to the organoleptic and chemical attributes of wine because of their interaction with other phenolic compounds (*9*, *10*) as well as with proteins and polysaccharides (*11*).

Recently, a great deal of interest in anthocyanins has emerged because of their potential health benefits as antioxidant, anti-inflammatory, antiaggregative, and vasodilating agents (*12*−*16*).

The major anthocyanins encountered in grapes of the species *Vitis vinifera* are reported in **Figure 1**. They are divided into five classes depending of their aglycon (anthocyanidin), that is, derivatives of delphinidin, cyanidin, petunidin, peonidin, and malvidin. The anthocyanins in grape skins are predominately 3-*O*-monoglucosides. The glucose residue may be acyled with acetic, *p*-coumaric, or caffeic acid (*8*).

The accumulation of anthocyanins in grape berries in a number of cultivars (Tempranillo, Cabernet Sauvignon, Merlot, and Cabernet Franc) at different stages of ripening has been previously investigated by several authors (*3*, *4*, *17*−*21*). However, no papers have addressed the impact of agronomic practices (organic versus conventional production) on the anthocyanin content in grape berries.

Few available studies have compared nutrient compound content in a given crop grown under conventional or organic production system.

Some studies on the phenolic composition of fruits from conventional or organic production are available mainly on apples (*22*), strawberries (*23*), pineapples (*24*), and prunus (*25*) but not yet on grape berries. Despite the heterogeneity of the sample material, some differences in health-promoting compound levels between foods from conventional and organic agricultural practice have been identified (*26*). Lombardi-Boccia et al. (*27*) examined polyphenol contents in yellow plums from organic and conventional production. Here, it was shown that products from conventional practice had higher contents of polyphenols. On the other hand, higher antioxidant microcon-

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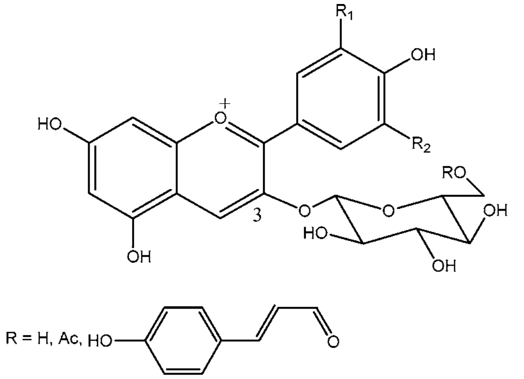

Anthocyanin	R_1	R_2	R
I : delphinidin 3-O-glucoside	OH	OH	H
II: cyanidin 3-O-glucoside	OH	H	H
III: petunidin 3-O-glucoside	OCH_3	OH	H
IV: peonidin 3-O-glucoside	OCH_3	H	H
V: malvidin 3-O-glucoside	OCH_3	OCH_3	H
VI: peonidin 3-O-(6-O-acetyl)glucoside	OCH_3	H	acetyl
VII: malvidin 3-O-(6-O-acetyl)glucoside	OCH_3	OCH_3	acetyl
VIII: peonidin 3-O-(6-O-*p*-coumaryl)glucoside	OCH_3	H	*p*-coumaryl
IX: malvidin 3-O-(6-O-*p*-coumaryl)glucoside	OCH_3	OCH_3	*p*-coumaryl

Figure 1. Structures of anthocyanins analyzed in the samples tested.

stituent levels (i.e., vitamin C, carotenoids, and polyphenols, except chlorogenic acid) were found in organic tomatoes than in conventional tomatoes (when results were expressed as fresh matter) (*28*).

The aim of our study was to evaluate by high-performance liquid chromatography (HPLC) the influence of different agronomic practices on the anthocyanin accumulation in Syrah grape skins collected at different stages of ripening over one season.

MATERIALS AND METHODS

Vineyards. Samples of Syrah grapes were collected in 2002 from two experimental plots close to Chateauneuf-du-Pape, Vaucluse, France. The experimental vineyards were 10 km apart but were located on the same characteristic terroir of the Chateauneuf-du-Pape appelation. This distinctive soil is characterized by large round quartz stones known as “galets” mixed with sandy red clay. The selection of neighboring parcels allowed us to compare organic and conventional vineyards in the same climate and soil conditions.

Organic grapes were treated with natural pesticides such as dry flowable sulfur, copper salts (reduction of application compared to official doses), oligoelements, and marine algae as stimulative of growth. The fertilizing process was based on a compost of sheep manure and grape marc. Conventional production used fertilizers and pesticides to control weeds, pests, and diseases; these chemicals are subject to rigorous testing and authorization procedures before they can be used, and winegrowers have to respect precise guidelines and restrictions to use them.

The grapes were collected at seven different stages of ripening: the sampling took place from veraison (July 22) to full maturity (September 13). Two hundred berries were randomly taken from each sample. Samples were immediately frozen and stored at −20 °C until chemical analyses were performed. Nine anthocyanins from the skin of grape berries were analyzed by HPLC for each sample of each parcel.

Chemicals. All solvents and acids used were of HPLC grade purchased from VWR International (Darmstadt, Germany). Malvidin 3-*O*-glucoside chloride was purchased from Extrasynthese (Lyon, France).

Extraction Procedure. Crude anthocyanin extracts were obtained according to the method of Roggero (*3*). Skins from 50 frozen berries were separated manually from the pulp and seeds and homogenized in an Ultra Turrax apparatus for 2 min in acidified methanol (0.1% HCl). The resulting slurry was filtered through a Whatman no. 1 filter paper in a Büchner funnel and concentrated in a rotary vacuum evaporator at a temperature below 35 °C. The crude skin extract was filtered through a 0.2 μm cellulose regenerated filter (Alltech Associates, Deerfield, IL) prior to HPLC analysis.

HPLC Analysis. HPLC analyses were performed using a Waters (Milford, MA) HPLC system consisting of a Waters 600E pump, a Waters 717 autosampler, a Waters 996 photodiode array detector, and a Millenium workstation.

The chromatographic separation was carried out on an Alltech Prevail C18 column (250 × 4.6 mm, 5 μm particle size) and a guard column of the same material. The solvents were (A) water/formic acid (90:10) and (B) acetonitrile/water/acid formic (30:60:10). The gradient was linear at a flow rate of 1 mL/min, and the following proportions of solvent B were used: 0−40 min, 20−76%, 40−60 min, 76−90%; 60−67 min, 90−100%. Detection was carried out at 530 nm. Identification of anthocyanins was obtained by comparing the elution order and UV and visible spectra with those found in the literature (*29*, *30*). Quantification was carried out by using the external standard method. Because standards for all of these compounds were not available, all anthocyanin compounds have been expressed as malvidin 3-*O*-glucoside equivalents (mg of Mv-3-Glc/L), which was used as the standard. All analyses were made in triplicate.

RESULTS AND DISCUSSION

Changes in Total Anthocyanins. Figure 2a shows changes in total anthocyanins in grape skin extracts from Syrah berries collected during ripening in 2002 and grown by conventional (CP) or organic (OP) agricultural practices.

The content of total anthocyanins for both vineyards achieved a maximum 28 days after veraison and then decreased until harvest. These data are consistent with the findings of Somers et al. (*31*) and Roggero et al. (*3*) showing that a maximal anthocyanin content in Syrah grapes was reached 20−30 days

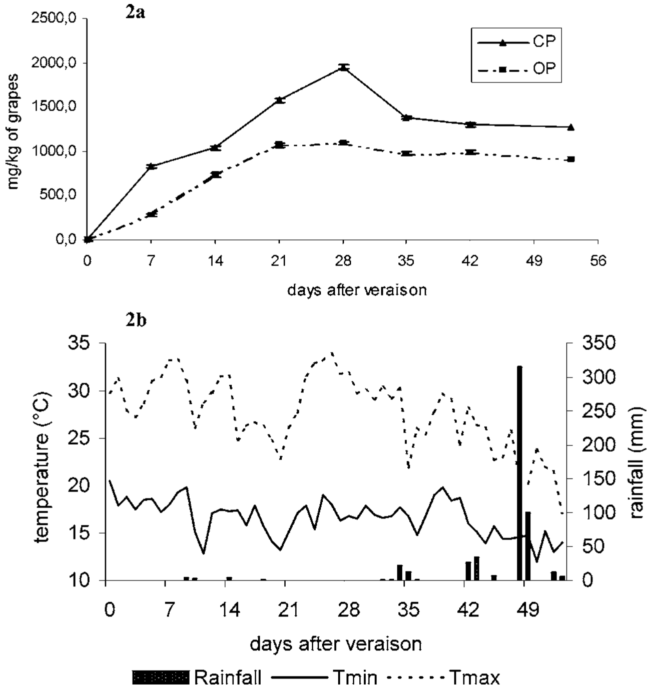

Figure 2. Total anthocyanins in grape skins (mg/kg of grapes) from veraison to harvest in each vineyard (**a**) and climatic conditions of 2002 season (**b**).

after veraison followed by a decline. However, small qualitative changes were observed even after 50 days from veraison.

The increase in anthocyanin concentration in the skin coincided with the many processes taking place as stage III (veraison) begins, such as the increase in berry deformability, the loss of chlorophyll, and the accumulation of sugar in the skin of black and red cultivars (*32*).

The anthocyanin concentrations were very high for both plots, which reflects the enological potential of the Syrah grapes and the hot climatic conditions in 2002 that favored anthocyanin biosynthesis during maturation. **Figure 2** shows that the accumulation of anthocyanins in grape skin was related to elevated temperature. Indeed, days with temperature >30 °C during the veraison−harvest period were correlated to an accumulation of phenolics (*33*, *34*). Additionally, the water deficits over 47 days after veraison probably enhanced anthocyanin formation in red grape varieties. Nevertheless, conventionally grown grapes showed a significantly higher content of total anthocyanins compared to that found in the organic cultivation. Several groups (*25*, *35*) have hypothesized that plants under organic production produce higher levels of polyphenols because they suffer higher pest-related stress due to the prohibition against applications of synthetic pesticides.

In our case, the exceptionally dry and hot weather of this season probably caused a weaker pathogen pressure in plots. Thus, the stress possibly triggered by the spraying of synthetic chemicals and the abundant use of copper salts on conventionally grown grapes could have been stronger than the pathogenic pressure. The response of the plants, in particular of the grapevine, to certain synthetic chemical treatments such as systemic fungicides or other pesticides used currently showed similarities with the "hypersensitive reaction" developed at the time of the fungal attack (*36*, *37*). The same secondary products are often formed as phytoalexins and "stress metabolites" (*38*), such as anthocyanins. Hence, accumulation of anthocyanins in conventionally grown grapes could be a mechanism of plant response to a chemical stress such as pesticide spraying.

Changes in the Content of Individual Anthocyanins during Ripening. Nine anthocyanins [3-*O*-monoglucosides of delphinidin, cyanidin, petunidin, peonidin, and malvidin, malvidin 3-*O*-(6-*O*-acetyl)glucoside, malvidin 3-*O*-(6-*O*-*p*-coumaryl)glucoside, peonidin 3-*O*-(6-*O*-acetyl)glucoside, and peonidin 3-*O*-(6-*O*-*p*-coumaryl)glucoside] were identified in the skin extracts.

Five anthocyanins (**I**−**V**) were present from veraison to full maturity. The concentration of these anthocyanins in CP skins rose continuously over the 28 days following veraison, then dropped during 7 days, and finally remained almost constant until the end of ripening. Cyanidin 3-*O*-glucoside (**Figure 3**), delphinidin 3-*O*-glucoside (**Figure 4**), petunidin 3-*O*-glucoside (**Figure 5**), and malvidin 3-*O*-glucoside (**Figure 7**) contents in OP skins increased over the 21 days following veraison and then slightly decreased until harvest except for the content of cyanidin 3-*O*-glucoside, which raised again 42 days after veraison. Peonidin 3-*O*-glucoside (**Figure 6**) showed two maxima at days 28 and 42 after veraison.

The contribution of cyanidin 3-*O*-glucoside to the total anthocyanin concentration ranged from 1 to 4% in CP and from 4 to 13% in OP (**Figure 3**), whereas that of delphinidin 3-*O*-glucoside ranged from 9 to 14% in CP and from 5 to 16% in OP (**Figure 4**). The contribution of peonidin 3-*O*-glucoside (**Figure 6**) was very different, ranging from 18 to 25% in OP and from 9 to 13% in CP. Finally, the contribution of petunidin 3-*O*-glucoside (**Figure 5**) was between 5 and 11% in OP and between 9 and 14% in CP, whereas the contribution of malvidin 3-*O*-glucoside was between 20 and 35% in OP and between 37 and 43% in CP (**Figure 7**).

In other words, malvidin 3-*O*-glucoside was always present in the highest proportion of the total anthocyanin concentration throughout ripening, followed by delphinidin 3-*O*-glucoside, petunidin 3-*O*-glucoside, and peonidin 3-*O*-glucoside, which have practically the same contribution except for the OP, in which case peonidin 3-*O*-glucoside is the second anthocyanin,

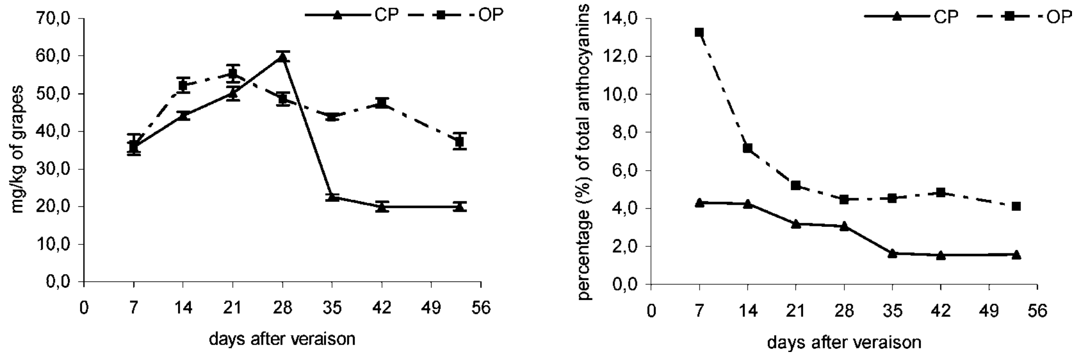

Figure 3. Changes in cyanidin 3-*O*-glucoside content during ripening in milligrams per kilogram of grapes or in percentage of total anthocyanins.

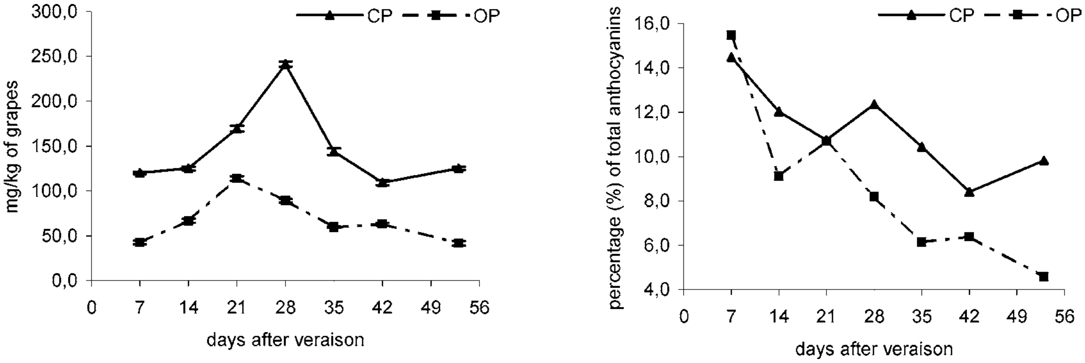

Figure 4. Changes in delphinidin 3-*O*-glucoside content during ripening in milligrams per kilogram of grapes or in percentage of total anthocyanins.

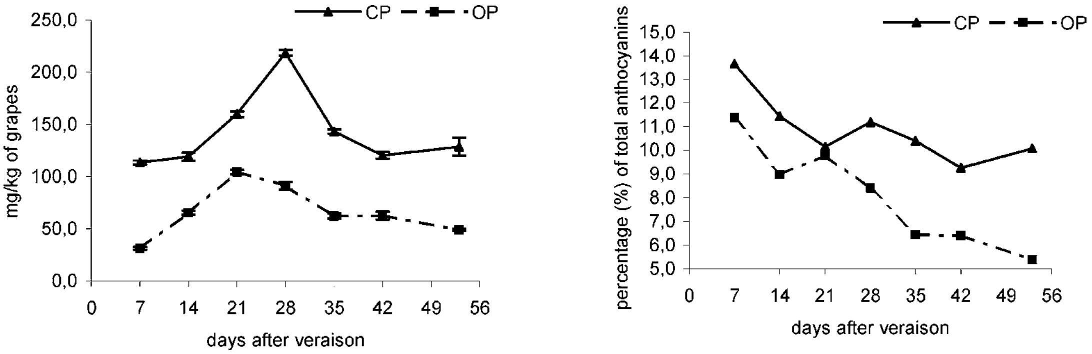

Figure 5. Changes in petunidin 3-*O*-glucoside content during ripening in milligrams per kilogram of grapes or in percentage of total anthocyanins.

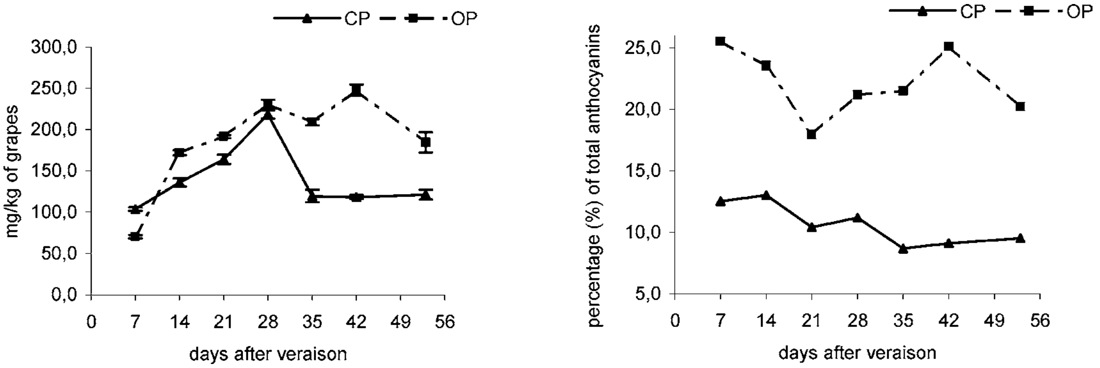

Figure 6. Changes in peonidin 3-*O*-glucoside content during ripening in milligrams per kilogram of grapes or in percentage of total anthocyanins.

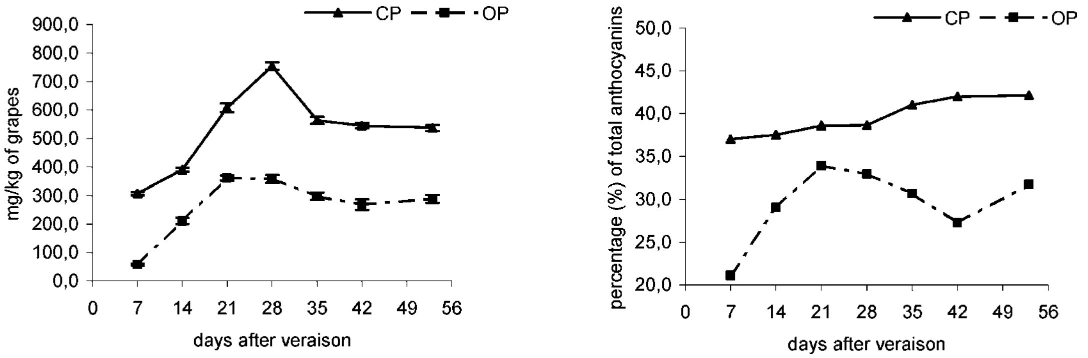

Figure 7. Changes in malvidin 3-*O*-glucoside content during ripening in milligrams per kilogram of grapes or in percentage of total anthocyanins.

and finally cyanidin 3-*O*-glucoside, which was the lowest for both. These findings agreed with values reported by Gonzalez (*39*), who found that in *Vitis vinifera* L. cv. Tempranillo grape skins, malvidin 3-*O*-glucoside was the major anthocyanin throughout ripening, whereas cyanidin 3-*O*-glucoside was the pigment present in the lowest proportion. In addition, our results were consistent with those published by Roggero (*3*) and coworkers, who reported similar trends.

During anthocyanin biosynthesis, primitive pigments (cyanidin 3-*O*-glucoside and delphinidin 3-*O*-glucoside) are converted into more stable pigments via methylation catalyzed by 3′-*O*-methyltransferase. Hence, delphinidin 3-*O*-glucoside is successively converted into petunidin 3-*O*-glucoside and malvidin 3-*O*-glucoside. Peonidin 3-*O*-glucoside and malvidin 3-*O*-glucoside represent the ultimate structures in the chain of anthocyanin biosynthesis. Esteban et al. (*40*) explained that the abundance

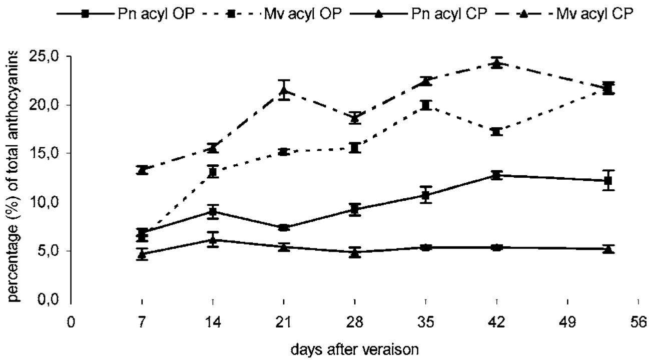

Figure 8. Changes in acylated pigments during ripening in percentage of total anthocyanins.

of peonidin 3-*O*-glucoside and malvidin 3-*O*-glucoside in grapes is an indicator of the biological activity of the plant considered. These data could explain the elevated peonidin 3-*O*-glucoside content that we found in organically grown grapes.

The most abundant acylated anthocyanins in Syrah grape skins are acetyl and *p*-coumaryl derivatives of malvidin 3-*O*-glucoside (**VII** and **IX**). Taken together, they contributed to the total anthocyanin content by 5−25% in CP and by 7−20% in OP during maturation (**Figure 8**). The contribution of acylated peonidin 3-*O*-glucosides (**VI** and **VIII**) to the total anthocyanin concentration was almost constant for conventionally grown grapes (≈5%).

Conclusion. On most sampling dates, anthocyanin concentrations were observed to be higher in the skins from conventionally grown berries compared with berries from organic production. For the grape variety considered, climatic conditions and agronomic practices were all important factors contributing to the changes in anthocyanin contents.

In organic production, synthetic chemicals (fertilizers and pesticides) that are used in conventional production are not allowed. Therefore, organically grown plants are usually exposed to different forms of stress, which induce accumulation of phenolic compounds. However, during the especially dry and hot summer of 2002, chemical stress accompanying conventional production probably overtook biotic stresses such as pest pressure, finally resulting in a higher anthocyanin content in grape skin. These unexpected findings may be significant in the current debate about the possible benefits of conventionally grown versus organic foods.

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