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Regional characteristics of anthocyanin and flavonol compounds from grapes of four *Vitis vinifera* varieties in five wine regions of China

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ABSTRACT

Anthocyanins and flavonols are important flavonoid metabolites in grapes, making a dominant contribution to the color, the mouth feel and even the flavor of grapes and wines. The accumulation of these flavonoids in grapes is greatly influenced by a many, diverse but interacting factors, of which variety and climate are among the most important ones. In the present study, the anthocyanin and flavonol profiles of four grape varieties (*Vitis vinifera* L.), Cabernet Sauvignon, Carmenere, Syrah and Merlot, from five major wine regions in China were examined for two consecutive years (2006 and 2007). The results showed that the total anthocyanin content of the berry skins in these cultivars tended to increase from east to west in China, yet the proportion of the acylated anthocyanins displayed the opposite trend. It seemed possible that the western grape regions, with their high altitude and low annual rainfall, had an advantage in producing high level of anthocyanins. In addition, a high proportion of trihydroxylated flavonols were always found in the western region grapes, whereas dihydroxylated flavonols were more prominent in the lower altitude eastern regions. This suggested that the relative amounts of these flavonoid compounds may depend on their corresponding cultivar characteristics, while the amounts are more affected by the environmental factors where they were growing.

1. Introduction

Vitis vinifera grapes, both for fresh consumption and wine, are an important source of phenolic compounds for humans. Based on their carbon skeleton, phenolics can be divided into two main groups: flavonoids (anthocyanins, flavonols and flavan-3-ols) and non-flavonoid compounds (stilbenes, hydroxybenzoic and hydroxycinnamic acids). Among the flavonoids of grape berries, anthocyanins and flavonols in

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particular are responsible for wine's major organoleptic properties, such as color and taste (García-Puente Rivas, Alcalde-Eon, Santos-Buelga, Rivas-Gonzalo, & Escribano-Bailón, 2006; González-Manzano, Dueñas, Rivas-Gonzalo, Escribano-Bailón, & Santos-Buelga, 2009; Pérez-Magariño & González-San José, 2006). Synthesized after veraison, anthocyanins are the main reason for the development and change in color during the development of berry ripening, and then normally degrade or transform into more stable pigments during wine aging (Bakker et al., 1997; García-Puente Rivas et al., 2006). Flavonols contribute to bitterness, and also play critical roles in color stabilization as cofactors with free anthocyanins in copigmentation of young red wines, and in the evolution of complex pigments during wine aging (Gómez-Míguez et al., 2006; González-Manzano et al., 2009; Liang et al., 2012).

Wine quality depends not only on enological practices, but more importantly also on the quality of the grapes used. As we know, besides the intrinsic varietal characteristics many external environmental factors, such as climate, soils and viticultural practices can also strongly influence the quality of the harvested grapes. Therefore, in the past few decades, many viticultural researchers have focused on the influence of the grape growing environment. According to Price, Breen, Valladao, and Watson (1995) and Spayd, Tarara, Mee, and Ferguson (2002), a positive correlation was found between sunlight exposure and an increase of flavonol content in Pinot Noir and Merlot grapes. Downey, Harvey, and Robinson (2004) reported that reduced biosynthesis rather than degradation was responsible for the low levels of flavonols present in shaded grapes, and that flavonol biosynthesis in Syrah berries was induced by light. Downey, Dokoozlian, and Krstic (2006) also suggested that flavonoid biosynthesis in plants generally was affected by numerous factors including light, temperature, altitude, soil type, water, microbial interactions and nutritional status. In detail, some enzymes, particularly those in the anthocyanin biosynthetic pathway, appear to be regulated in part by UV radiation and in part by the phytochrome-activating wavelengths of 200–400 nm (Meyer, Pepin, & Smith, 2002). There are also significant characteristic differences on the flavonoid profiles among grape cultivars. For example, in *V. vinifera* grapes anthocyanidins are usually monoglucosylated with malvidin or peonidin derivatives being the highest anthocyanins (García-Beneytez, Cabello, & Revilla, 2003). Conversely, the anthocyanidin 3,5-*O*-diglucosides are primarily observed in non-*vinifera* species such as *Vitis labrusca* (Concord grapes) with delphinidin being the highest in overall abundance (McCallum, Yang, Young, Strommer, & Tsao, 2007). Furthermore, the contents and proportions of anthocyanin derivatives are obviously different with varieties. According to González-Neves et al. (2007), the results obtained found that the anthocyanic contents of Tannat (*V. vinifera*) were significantly higher than Merlot and Cabernet-Sauvignon, allowing the accumulation of delphinidin and petunidin derivatives. Merlot (*V. vinifera*) seemed to allow the preferential accumulation of peonidin derivatives in the skins while the highest accumulation of malvidin derivatives existed in Cabernet Sauvignon with higher acetylated forms.

In recent years in China, there has been a rapid expansion of grape growing, particularly for wine production. Most of this has been concentrated in the north and northwest regions, in the vicinity of 38°N. In terms of longitude China spans from 73°E to 135°E, a distance of some 4900 km. The climatic conditions vary greatly with increasing altitude and distance from the ocean from east to west, which might impact the accumulation of flavonoid compounds in grapes. The present work compares the anthocyanin and flavonol profiles of four *V. vinifera* grape varieties harvested from vineyards typical of five major wine regions in China. This was done to help to evaluate the varietal potential of China's different regions and to expand our knowledge of the impact of environmental factors on the grape flavonoid accumulation.

2. Materials and methods

2.1. Chemicals and standards

The standards of malvidin-3-*O*-glucoside and quercetin were purchased from Sigma-Aldrich Co. (St. Louis, MI, USA). Methanol, formic acid, acetonitrile and acetic acid (HPLC grade) were obtained from the Fisher Company (Fairlawn, NJ, USA). Ethyl acetate (analytical grade) was obtained from Beijing Chemical Reagent Plant (Beijing, China). Deionized water (<18 MΩ resistance) was obtained from a Milli-Q Element water purification system (Millipore, Bedford, MA, USA).

Table 1
Regional climate, soil type and the grape cultivar details from five representative vineyards in the regions studied.

Grape grown region	Regional soil type	Cultivars	Regional climate condition
Qilian of Gansu (GSQL)	Sandy soils	Cabernet Sauvignon (06ql-1, 06ql-2, 07ql) Carmenere (06pl-1, 06ql-2, 07ql-1, 07ql-2) Syrah (06ql, 07ql) Merlot (06ql, 07ql-1, 07ql-2)	The vineyards (99°84′ E, 39°14′ N) are located on the desert edge zones at an altitude of about 1214 m with a cool–arid continental monsoon climate and abundant sunshine; with an annual rainfall of 66.4–104.4 mm and a big temperature difference between daytime and night time.
Yuquanying of Ningxia (NXYQY)	Gravelly soils	Cabernet Sauvignon (06yc, 07yqy, 07v) Carmenere (06yc, 07xxwl)	The vineyards (106°13′ E, 38°28′ N) are located on the alluvial plain and in the east of Helan mountain at an altitude of 1036 m with a semi-arid temperate continental climate and an annual sunshine time of about 3029 h; with an annual rainfall of 150–200 mm and a big temperature difference between daytime and night time.
Huanlai of Hebei (HBHL)	Brown and sandy soil	Cabernet Sauvignon (06ds, 07ds, 06yb) Syrah (06zf, 07zf) Merlot (06yb, 07hy, 07ds)	The vineyards (115°54′ E, 40°4′ N) are located on the plain around the two mountains of Yanshan and Taihang Mountain at the average altitude of 569 m; with a temperate continental monsoon climate and special microclimate area; with an annual sunshine time of 3072 h and an annual rainfall of about 413 mm.
Changli of Hebei (HBCL)	Clay and sandy soils	Cabernet Sauvignon (07hb, 07hw, 07h865, 07hpo, 07hpi) Syrah (06hx, 07hx)	The vineyards (118°85′ E, 39°89′ N) are located on the plain and adjacent to the Bohai Sea and Yanshan at an altitude of 212 m; with a cool–warm, semi-humid continental monsoon climate, an annual sunshine time of 2600–2800 h and an annual rainfall of 725 mm.
Penglai of Shandong (SDPL)	Sandy soils	Cabernet Sauvignon (06pln, 06plm, 07plx) Carmenere (06pl, 07pl)	The vineyards (120°75′ E, 37°8′ N) are located in the north of Jiaodong Peninsular and close to the Bohai Sea and Yellow Sea at the altitude of 39 m with an continental monsoon climate; with an annual sunshine time of above 2825 h and an annual rainfall of 664 mm.

The code of each cultivar in the parentheses was composed of the harvest year and the acronym lowercases of the grape-growing regions. The harvest years included 2006 (abbreviated 06) and 2007 (abbreviated 07).