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Anthocyanin characteristics of wines in *Vitis* germplasms cultivated in southern China

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Abstract

The anthocyanin profiles and CIELAB color values of nine wines in *Vitis* germplasms from southern China were compared. The results showed that the anthocyanin composition of wines from one hybrid between *V. vinifera and V. labrusca* ('Moldova'), two *V. labrusca* varieties ('Conquistador' and 'Saint-Croix'), one *V. quinquangularis* variety ('Yeniang No.2'), one hybrid between *V. quinquangularis* and *V. vinifera* ('NW196'), one *V. davidii* variety ('Xiangniang No.1') and one *V. rotundifolia* variety ('Noble') were dominated by anthocyanidin 3,5-*O*-diglucosides. All these were quite different from *V. vinifera* wines ('Cabernet Sauvignon' and 'Marselan'), which were characterized by the monoglucoside and pyranoanthocyanins. 3',4',5'-substituted anthocyanins were dominant in the wines of all varieties, except 'Noble' wine. 'Yeniang No.2' (*V. quinquangularis*) had the highest acid, total anthocyanin concentration, and showed a more intense pigmentation with a higher proportion and concentration of coumaroylated anthocyanins. In the colorimetric analysis, 'Yeniang No.2' (*V. quinquangularis*) wine showed the most saturated red colors, followed by 'NW196' (*V. quinquangularis*). The detected chromatic characteristics of these wines were basically in accordance with their sensory evaluation.

Keywords: anthocyanin; wine; HPLC-MS; *V.* germplasm; variety.

Practical Application: Perfecting evaluation system of the anthocyanin characteristics of nine wines in different *V.* germplasm from southern China.

1 Introdution

China is very abundant in *Vitis* germplasms resources, which are distributed around the country. *V.* davidii and quinquangularis are two of native species in China, harboring strong disease resistance and good adaptability to local humid-warm climate. *V. davidii* grapes were originally grown in subtropical areas, their mature berries have thick dark-red skins. The wines produced from *V. davidii* grapes present dark purple or ruby red color and have typical of the varieties with the aroma (Liang et al., 2013). The ripened berries of *V. quinquangularis* have a low sugar content, high acid and dark-colored skins. The wines are characterized by pronounced acid and tannic taste (Zou et al., 2012). In addition, cultivation of *V. labrusca*, *V. vinifera*× *V. labrusca* and *V. rotundifolia* grapes have been expanding in the south of China due to their strong disease, pest resistance and stress tolerance during the past decades (Jing, 1999).

Anthocyanins are pigments located in the grape skins, which are responsible for the red colouration of the berries and subsequent wines (Ribéreau-Gayon & Glories, 1986). Genetic backgrounds are determining factor for anthocyanin profile of each variety, thus the anthocyanin compositions have been used as "finger prints" for the varietal differentiation of the grapes and wines (Liang et al., 2008). *V. vinifera* grapes consist of only anthocyanin-monoglucoside (García-Beneytez et al., 2002; Liang et al., 2008), while *V. labrusca* and *V. rotundifolia* contain not only anthocyanin monoglucoside but also anthocyanin diglucosides (Liang et al., 2008; Huang et al., 2009). Moreover, the wines produced from these species also have corresponding anthocyanin composition (Huang et al., 2009).

During the past several decades, some wine grape varieties obtained from the wild grapes native to China, and these varieties were rich in phenolics and showed strong disease resistance (Zou et al., 2012; Wu et al., 2013). Although several previous studies on wild grape germplasms of China have dealt with the anthocyanin composition and content (Liang et al., 2008, 2013), few studies have focused on the anthocyanin profiles of wines in these *V.* germplasms. In the present paper, the composition and content of anthocyanins of the nine wines in *V.* germplasms from southern China was investigated by means of HPLC- MS, with an aim of leading to a perfect evaluation system of wine quality in Chinese grape germplasms and a better understanding of relationship between wine color and anthocyanin profiles.

2 Materials and methods

2.1 Grape varieties

Nine grape varieties were investigated in this study, which included two *V. vinifera* varieties ('Cabernet Sauvignon' and 'Marselan'), one hybrid between *V. vinifera* and *V. labrusca* ('Moldova': GuzaliKala×SV12375), two *V. labrusca* varieties ('Conquistador' and 'Saint-Croix'), one *V. quinquangularis* variety ('Yeniang No.2'), one hybrid between *V. quinquangularis* and *V. vinifera* ('NW196': 83-4-96×Мускат Розовый), one *V. davidii*

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variety ('Xiangniang No.1') and one *V. rotundifolia* variety ('Noble'). All the grapes were grown in Guangxi, a province in southern China. All vines of nine varieties cultivated with rain-shelter, and the grapes were hand harvested at technological ripeness in 2015. More information of plant materials are shown in Table S1 (Appendix A).

2.2 Small-scale winemaking

Following the National Standard of the People's Republic of China-GB/T 15038-2006 (China National Institute of Standardization, 2006), chemical characteristics of grape berries from nine varieties were illustrated in Table S2. Grapes were crushed on an experimental destemmer-crusher and then transferred to glass containers. A total volume of 60 L of each variety wine was produced in three replicates (20 L per replicate), and 20 g/ton pectinase and 30 mg/L SO_2 were added to the musts. After maceration of the musts for 24 h, 200 mg/L of dried active yeast (Lalvin 71B, France) were added to the musts, according to commercial specifications. Alcoholic fermentation was carried out at 25 °C to dryness (reducing sugar < 4 g/L), and density controls were maintained during this period. All fermentations for each variety were completed within 10 days. At the end of alcoholic fermentation, residual sugar, pH and ethanol were analyzed according to official OIV practices, and were illustrated in Table S3 (Office International de la Vigne et du Vin, 1990). After fermentation, the wine samples were bottled and stored at 15 °C prior to analysis.

2.3 Chemical analysis and chromatic characteristics of wines

At the end of alcoholic fermentation, spectrophotometric measurements of absorbance at 440, 530, and 600 nm were conducted by using a 1 mm quartz cuvette. The CIELAB parameters (L*, a*, b*, C*, h) were calculated by the absorbance values at 440, 530, and 600 nm (Ayala et al., 1999).

2.4 Wine tasting

A wine tasting experiment was held when the wine samples were bottled at 15 °C for six months. The tasting team was composed of ten professional panelists, who were either working in the wine industry or national wine taster. Wine samples were stored at 15°C and presented at 25°C for tasting. The tasting scores were defined according to the methods of Tao et al. (2009).

2.5 HPLC-MS analyses of anthocyanins

The detection of anthocyanins was carried out according to the previously published method of Liang et al. (2013).

2.6 Statistical analysis

All analyses were expressed as means ± standard deviations (S.D.) of triplicate. Significant differences were determined at $p<0.05$, according to Duncan's multiple range tests. Cluster analysis of total anthocyanin and individual anthocyanin concentration in wines from different varieties was performed by Metabo-Analyst 3.0. Excel 2010 (Microsoft Corp., Redmond, WA, USA) were used to draft the graph.

3 Results and discussion

3.1 Colorimetric analysis of wines

In this study, the total color differences of nine wines were monitored in the CIELAB color space system (Table 1). 'Yeniang No.2' wine showed the most saturated red colors (highest values of *C** and *a**), which followed by 'NW196'. 'Xiangniang No1' wine appeared the lowest chroma and red color (lowest values of C* and a*). 'Conquistador' and 'Saint-Croix' wines had lower values of C* and a* than that made by 'Moldova'. With respect to the yellow-blue color b* and hue h, 'Moldova' produced wine with most blue hue (lowest value of b* and h), whereas 'Noble' and 'Cabernet Sauvignon' wines showed more yellow color (higher value of b* and h). The detected chromatic characteristics of the wines were basically in accordance with their different sensory evaluation.

3.2 Descriptive analysis (DA)

Descriptive Analysis was used to quantitatively characterize differences in the perceived organoleptic profiles of the wines made from varieties grapes (Figure 1). Xiangniang No.1 wine displayed more ruby than violet in hue with the lowest color depth. 'Noble', 'Conquistador' and 'Cabernet Sauvignon' wines also showed more ruby in hue, but 'Marselan', 'Moldova', 'Saint-Croix', 'Yeniang No.2' and 'NW196' had red-violet color with blue tones. 'Yeniang No.2' had the highest color depth among all the wines, meanwhile, it was much sourer than the other wines. In addition, 'NW196' wine also had higher score of acid. These results could be attributed to higher titratable acidity content in 'Yeniang No.2' and 'NW196' wines and grapes (Table S2; Table S3). Wines made from *V. vinifera* grapes were perceived as higher alcohol, and its finish were longer than the other variety wines. The finishes of 'Moldova' and 'Noble' wines were shorter than the other wines.

Among thirty-six anthocyanins found in nine varieties wines (Table 2), twelve of these are 3, 5-*O*-diglucosides. All of them were detected in 'Moldova' (M), 'Conquistador' (C), 'Saint-Croix' (SC), 'Yeniang No.2' (Y), 'NW196' (NW), 'Xiangniang No.1' (X), 'Noble' (N). These were quite different from *V. vinifera* wines ('Cabernet Sauvignon' and 'Marselan'), which were characterized by the monoglucoside and pyranoanthocyanins. However, grape species native to China, *V. quinquangularis* and *V. davidii*, have also been demonstrated to be rich in anthocyanidin diglucosides and acylated derivaties in their wines, without any pyranoanthocyanins being detected.

Via cluster analysis, these wines made by different varieties were broadly clustered into two groups according to their characteristic anthocyanin content and composition (Figure 2). Total anthocyanin concentrations of the wines decreased in the order: 'Yeniang No.2' > 'NW196' > 'Marselan' > 'Noble' > 'Saint-Croix' > 'Moldova' > 'Xiangniang No.1' > 'Cabernet Sauvignon' > 'Conquistador'. The differences in anthocyanin compositions of wines were obvious between *V. vinifera* and non-*V. vinifera* and also between the varieties

Table 1. Chromatic characteristics for wines[a].

	V. vinifera		V. vinifera×V. labrusca	V. labrusca		V. quinquangularis	V. quinquangularis × V. vinifera	V. davidii	V. rotundifolia
	Cabernet Sauvignon	Marselan	Moldova	Conquistador	Saint-Croix	Yeniang No.2	NW196	Xiangniang No.1	Noble
*L**	53.67 ± 1.00c	53.22 ± 0.75c	42.73 ± 0.81f	46.23 ± 1.79e	50.43 ± 1.52d	51.08 ± 0.19d	52.73 ± 0.33c	78.90 ± 0.11a	57.43 ± 0.64b
*C**	47.38 ± 0.77d	44.14 ± 0.56e	52.78 ± 0.58c	43.58 ± 1.26e	38.44 ± 0.92f	63.02 ± 0.07a	55.11 ± 0.12b	24.53 ± 0.23g	55.60 ± 0.56b
*a**	44.65 ± 0.71e	43.52 ± 0.52e	50.71 ± 0.52d	43.58 ± 1.26e	38.00 ± 0.90f	62.87 ± 0.08a	54.94 ± 0.12b	24.42 ± 0.23g	52.71 ± 0.39c
*b**	15.85 ± 0.32b	7.32 ± 0.30c	-14.64 ± 0.29i	0.51 ± 0.16g	5.81 ± 0.20d	4.37 ± 0.15e	-4.37 ± 0.03h	2.33 ± 0.08f	17.68 ± 0.59a
h	19.54 ± 0.11a	9.55 ± 0.28c	-16.10 ± 0.15i	0.67 ± 0.20g	8.69 ± 0.11d	3.98 ± 0.14f	-4.55 ± 0.03h	5.45 ± 0.24e	18.54 ± 0.46b

[a] Wine data were collected at the end of alcoholic fermentation. Data represent mean±standard error (n =3). In each row, mean values followed by different letters are significantly different ($p < 0.05$).

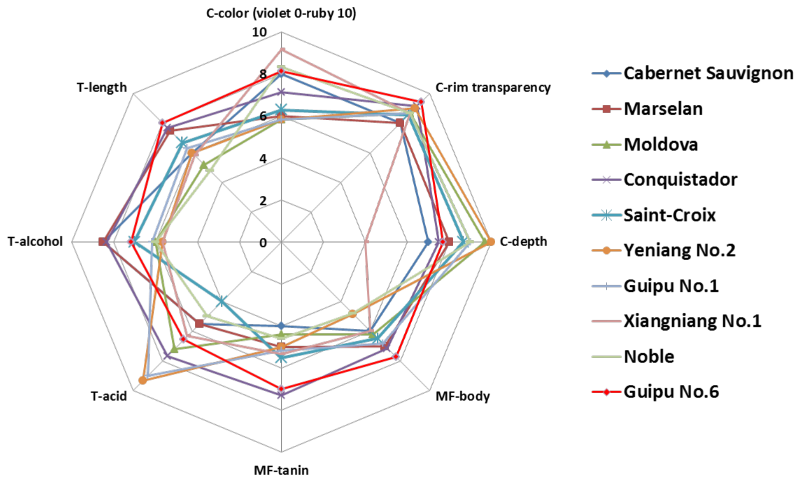

Figure 1. Polar coordinate (spider plot) graph of the mean intensity rating of sensory attributes for different varieties wines (C= color; T= taste; MF= mouthfeel).

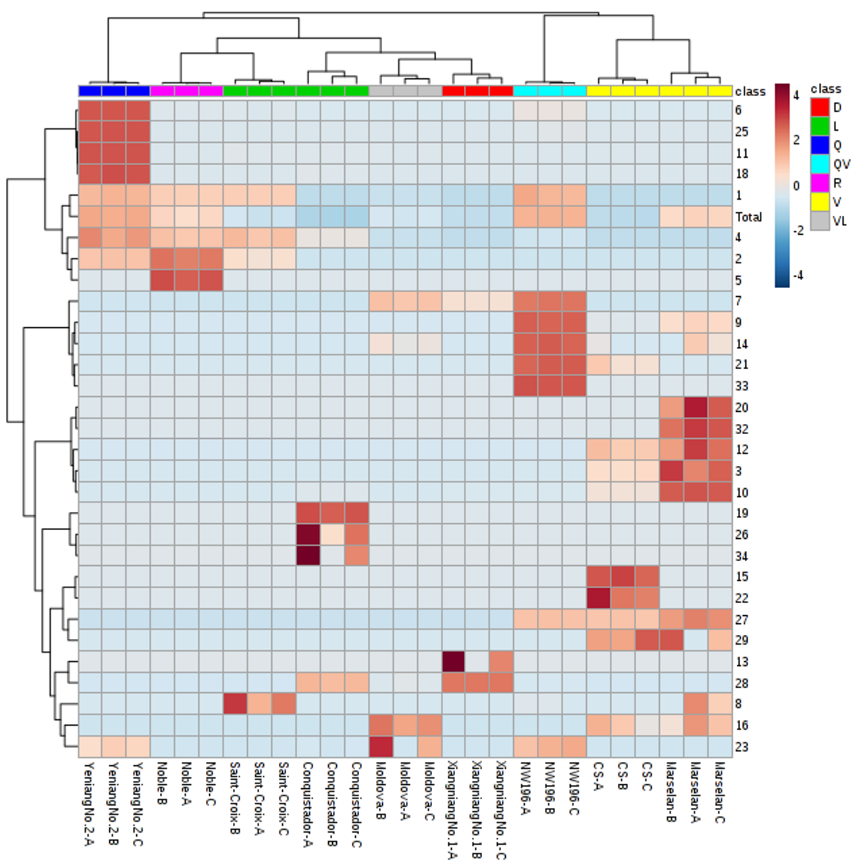

Figure 2. Cluster analysis of total anthocyanin concentration and concentration of each anthocyanin in wines. The capitals in parenthesis following the variety indicate the biological repeats. V: *V. vinifera*; VL: *V. vinifera*×*V. labrusca*; L: *V. labrusca*; Q: *V. quinquangularis*; QV: *V. quinquangularis*×*V. vinifera*; D: *V. davidii*; R: *V. rotundifolia*.

originating from East Asia and North America. *V. davidii* with multi-resistance and good agronomic traits is a kind of wild grapes native to subtropical areas in China (Liang et al., 2013). As regards *V. vinifera*, acylated monoglucosides and pyranoanthocyanins in 'Cabernet Sauvignon' and 'Marselan' wines were greater in abundance than the other species. Although "Wild *V. quinquangularis*" is one of parents of 'NW196', 'Yeniang No.2' (*V. quinquangularis*) wine exhibited significant difference in anthocyanin profiles with 'NW196' (Figure 2). Malvidin-3,5-*O*-diglucoside was the most significant anthocyanin for 'NW196' grape berries (Xu et al., 2011), and the same was true for the 'NW196' wine. 'Noble' wine was very rich in Cyanidin-3,5-*O*-diglucoside and Pelargonidin-3,5-*O*-diglucoside. In the 'Noble' grape skins, only six anthocyanidin

Table 2. The characteristics of the anthocyanins of chromatography and mass spectrometry found in wines[a].

Peak number	TR (min)	Molecular ion M+(m/z)	Fragment ions M(m/z)	Identity	Variety
1	3.42	627	465, 303	Delphinidin-3,5-*O*-diglucoside	M, SC, Y, NW, N
2	4.11	611	449, 287	Cyanidin-3,5-*O*-diglucoside	SC, Y, N
3	4.83	465	303	Delphinidin-3-*O*-glucoside	CS, MA,
4	4.23	641	479, 317	Petunidin-3,5-*O*-diglucoside	M, C, SC, Y, NW, N
5	5.12	595	433, 271	pelargonidin-3,5-*O*-diglucoside	N
6	5.40	625	463, 301	Peonidin-3,5-*O*-diglucoside	SC, Y, NW, N
7	6.55	655	493, 331	Malvidin-3,5-*O*-diglucoside	M, Y, NW, X, N
8	7.77	479	317	Petunidin-3-*O*-glucoside	CS, MA, SC, NW,
9	9.80	463	301	Peonidin-3-*O*-glucoside	CS, MA, C, NW
10	10.62	493	331	Malvidin-3-*O*-glucoside	CS, MA, C, Y, NW, X
11	11.27	773	611, 465, 303	Delphinidin-3-*O*-(6-*O*-coumaryl)-glucoside-5-glucoside	M, C, SC, Y, NW, X
12	11.90	507	303	Delphinidin-3-*O*-(6-O-acetyl)-glucoside	CS, MA
13	12.18	697	655, 493, 331	Malvidin-3-*O*-(6-*O*-acetyl)-glucoside-5-glucoside	X
14	13.02	561	339	Malvidin-3-*O*-glucoside-pyruvic acid	CS, MA, M, NW
15	13.67	491	287	Cyanidin-3-*O*-(6-*O*-acetyl)-glucoside	CS
16	14.42	517	355	Malvidin-3-*O*-glucoside-acetaldehyde	CS, MA, M
17	15.30	603	399	Malvidin-3-*O*-(6-*O*-acetyl)-glucoside-pyruvic acid	CS
18	15.97	757	595, 449, 287	Cyanidin-3-*O*-(*cis*-6-*O*-coumaryl)-glucoside-5-glucoside	C,Y
19	16.15	801	639, 493, 331	Malvidin-3-*O*-(*cis*-6-*O*-coumaryl)-glucoside-5-glucoside	C
20	16.31	521	317	Petunidin-3-*O*-(6-*O*-acetyl)-glucoside	MA
21	17.47	809	519, 357	Malvidin-3-*O*-glucoside-ethyl-(epi)catechin	CS, MA, NW
22	17.49	559	355	Malvidin-3-*O*-(6-*O*-acetyl)-glucoside-acetaldehyde	CS
23	17.90	787	625, 479, 317	Petunidin-3-*O*-(6-*O*-coumaryl)-glucoside-5-glucoside	M, C, SC,Y, NW, X
24	18.20	505	301	Peonidin-3-*O*-(6-*O*-acetyl)-glucoside	CS
25	18.73	611	303	Delphinidin-3-*O*-(*trans*-6-*O*-coumaryl)-glucoside	Y, NW
26	19.96	771	609, 463, 301	Peonidin-3-*O*-(*trans*-6-*O*-coumaryl)-glucoside	C,Y
27	20.04	535	331	Malvidin-3-*O*-(6-*O*-acetyl)-glucoside	CS, MA, NW
28	20.72	801	639, 493, 331	Malvidin-3-*O*-(*trans*-6-*O*-coumaryl)-glucoside-5-glucoside	M, C, Y, NW, X
29	21.20	707	399	Malvidin-3-*O*-(6-*O*-coumaryl)-glucoside-pyruvic acid	CS, MA
30	23.20	663	355	Malvidin-3-*O*-(6-*O*-coumaryl)-glucoside-acetaldehyde	CS, M
31	24.98	609	301	Peonidin-3-*O*-(*cis*-6-*O*-coumaryl)-glucoside	CS
32	24.81	639	331	Malvidin-3-*O*-(*cis*-6-*O*-coumaryl)-glucoside	MA
33	26.51	639	331	Malvidin-3-(*trans*-6-*O*-coumaryl)-glucoside	NW
34	28.28	579	417	Peonidin-3-*O*-glucoside-4-vinylphenol	C
35	28.52	609	447	Malvidin-3-*O*-glucoside-4-vinylphenol	CS, MA
36	31.00	651	447	Malvidin-3-*O*-(6-*O*-acetyl)-4-vinylphenol	MA

[a] The peak numbers in the table correspond to the peak order of HPLC chromatogram of anthocyanins in wines detected at 525 nm. CS, Cabernet Sauvignon; MA, Marselan; M, Moldova; C, Conquistador; SC, Saint-Croix; Y, Yeniang No.2; NW, NW196; X, Xiangniang No.1; N, Noble.

diglucosides were found as well as in 'Noble' wine, where Cyanidin-3,5-*O*-diglucoside was the most abundant in 'Noble' grape (Zhu et al., 2012).

3.3 Modification of anthocyanidin

Considering modification, the differences of anthocyanidin in nine wines were shown in Table 3. With regard to monoglucoside and diglucosides, there were significant differences among the wines of seven species. The monoglucoside was the only anthocyanin type in the wines of *V. vinifera* and all the detected anthocyanins in 'Noble' wine were diglucosides (Table 3). Moreover, the diglucosides were the dominant anthocyanin type in the wines of *V. vinifera*×*V. labrusca* (98.38%), *V. labrusca* (Conquistador: 87.95%; Saint-Croix: 98.08%), *V. quinquangularis* (97.43%), *V. quinquangularis*×*V. vinifera* (79.17%) and *V. davidii* (96.93%). Normally, anthocyanin diglucosides are more stable than their monoglucoside counterparts, but are more susceptible to browning and are less colored (Kim et al., 2010). Thus, the wines made by *V. vinifera* would show better aging potential than those produced by *V. labrusca*, *V. vinifera*×*V. labrusca*, *V. quinquangularis*, *V. quinquangularis*×*V. vinifera* and *V. davidii*.

According to the numbers of B-ring substituents of anthocyanidins, the anthocyanins detected could be divided into three groups: 4'-substituents (pelargonidin-derivatives), 3', 4'-substituents (cyanidin- and peonidin-derivatives) and 3',4',5'-substituents (delphinidin-, petunidin- and malvidin-derivatives). In the present study, 3', 4', 5'-substituted

Table 3. Differentiation of some red wines according to variety based on their anthocyanin composition[a].

		V. vinifera		*V. vinifera*× *V. labrusca*	*V. labrusca*		*V. quinquangularis*	*V. quinquangularis*× *V. vinifera*	*V. davidii*	*V. rotundifolia*
		Cabernet Sauvignon	Marselan	Moldova	Conquistador	Saint-Croix	Yeniang No.2	NW196	Xiangniang No.1	Noble
Glycosylation	Monoglucoside	100 ± 0a	100 ± 0a	1.62 ± 0.37f	12.05 ± 0.30c	1.92 ± 0.71f	2.57 ± 0.09e	20.83 ± 0.17b	3.07 ± 0.03d	0 ± 0g
	Diglucoside	0 ± 0g	0 ± 0g	98.38 ± 0.37b	87.95 ± 0.30e	98.08 ± 0.71b	97.43 ± 0.09c	79.17 ± 0.17f	96.93 ± 0.03d	100 ± 0a
B-ring Substituted	3’,4’,5’-substituent	93.21 ± 0.28d	97.33 ± 0.32c	100 ± 0a	98.52 ± 1.41b	80.59 ± 1.19f	64.47 ± 1.23g	91.00 ± 0.17e	100 ± 0a	33.19 ± 0.11h
	3’,4’-substituent	6.79 ± 0.28e	2.67 ± 0.32f	0 ± 0h	1.48 ± 1.41g	19.41 ± 1.19c	35.53 ± 1.23a	9.00 ± 0.68d	0 ± 0h	25.82 ± 0.09b
	4’-substituent	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b	40.99 ± 0.02a
Acylation	Non-acylated	47.18 ± 0.59h	70.67 ± 2.09e	96.92 ± 0.81b	56.22 ± 2.33g	98.54 ± 1.35a	63.45 ± 1.08f	88.59 ± 0.28c	72.40 ± 0.08d	100 ± 0a
	Acetylated	52.50 ± 0.56a	21.43 ±1.38b	0 ± 0d	0 ± 0d	0 ± 0d	0 ± 0d	10.08 ± 0.12c	0.19 ± 0.02d	0 ± 0d
	Coumaroylated	0.32 ± 0.10h	7.90 ± 0.72d	3.08 ± 0.81e	43.78 ± 2.33a	1.46 ± 1.35f	36.55 ± 1.08b	1.33 ± 0.16g	27.41 ± 0.19c	0 ± 0i
Methoxylation	Non-methylated	9.22 ± 0.27e	3.24 ± 0.28f	3.00 ± 0.32g	1.73 ± 1.26h	49.09 ± 1.59c	58.47 ± 2.08b	13.10 ± 0.88d	0.04 ± 0.00i	78.98 ± 0.48a
	Methylated	90.78 ± 0.27d	96.76 ± 0.28c	97.00 ± 0.32bc	98.27 ± 1.26b	50.91 ± 1.59f	41.53 ± 2.08g	86.90 ± 0.88e	99.96 ± 0.06a	21.02 ± 0.48h
Pyranoanthocyanin	Vitisin A	0.56 ± 0.32b	0.41 ± 0.38b	0.56 ± 0.23b	0 ± 0c	0 ± 0c	0 ± 0c	1.25 ± 0.01a	0 ± 0c	0 ± 0c
	Vitisin B	6.41 ± 1.58a	0.33 ± 0.21bc	1.05 ± 0.15b	0 ± 0c	0 ± 0c	0 ± 0c	0 ± 0c	0 ± 0c	0 ± 0c
	Vinylphenol adduct	0 ± 0b	0 ± 0b	0 ± 0b	0.05 ± 0.00a	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b	0 ± 0b
	Catechin adduct	2.32 ± 0.78a	0 ± 0c	0 ± 0c	0 ± 0c	0 ± 0c	0 ± 0c	1.85 ± 0.04b	0 ± 0c	0 ± 0c

[a] Wine data were collected at the end of alcoholic fermentation. Data represent mean±standard error (n =3). In each row, mean values followed by different letters are significantly different ($p < 0.05$).

anthocyanins were dominant in the wines of all the species, except *V. rotundifolia*, accounting for 33.19% of total concentration (Table 3). Moldova and Xiangniang No.1 only contained 3', 4', 5'-substituted anthocyanins, and 4'-substituents were detected only in 'Noble' wine. In addition, 'Yeniang No.2' was greater in abundance of 3', 4'-substituents than the other wines.

In the case of acylated anthocyanins, the acetylated derivatives were the most abundant ones in wines of *V. vinifera* and *V. quinquangularis*×*V. vinifera*, but very low in 'Xiangniang No.1' wine (Table 3). 'Moldova', 'Conquistador, 'Saint-Croix' and 'Yeniang No.2' wines only contained coumaroylated anthocyanins, in which no acetylated anthocyanins were detected. Zhu et al. (2012) concluded *V. vinifera* grapes contained significantly higher proportion of acetylated anthocyanins than non-*V. vinifera* grapes. Hence, the results in *V. vinifera* wines were consistent with those found in grape berries. Additionally, the proportion and concentration of acylated anthocyanins can shift the color. Specifically, the acetylated anthocyanins displayed a bathochromic effect shifting slightly toward an orange hue compared with non-acetylated derivatives, whereas the coumaroylated anthocyanins showed a hypsochromic effect shifting toward a purple hue (González-Neves et al., 2007). Thus, 'Yeniang No.2' wine studied here showed a more intense pigmentation (hyperchromic effect) with a higher proportion and concentration of coumaroylated anthocyanins.

Anthocyanins can also be classified into non-methylated (pelargonidin-, delphinidin- and cyanidin-derivatives) and methylated ones (Petunidin-, peonidin- and Malvidin-derivatives). The proportions of methylated anthocyanins in the wines decreased in the order: 'Xiangniang No.1' (99.96%) > 'Conquistador' (98.27%) > 'Moldova' (97.00%)> 'Marselan' (96.76%) > 'Cabernet Sauvignon' (90.78%) > 'NW196' (86.90%) > 'Saint-Croix' (50.91%) > 'Yeniang No.2' (41.53%) > 'Noble' (21.02%) (Table 3).

In red wines, pyranoanthocyanins originated from the reaction between anthocyanins and 4-vinylphenol, pyruvic acid (Vitisin A), acetaldehyde (Vitisin B) or vinyl-flavanols (Alcalde-Eon et al., 2004). The colour of pyranoanthocyanins is also more stable at varying pH values and against the bleaching effect of bisulfite than those of the anthocyanins (Alcalde-Eon et al., 2004). In the present study, there were not any types of pyranoanthocyanin detected in 'Saint-Croix', 'Yeniang No.2', 'Xiangniang No.1' and 'Noble' wines (Table 3). 'NW196' had significant higher proportions of Vitisin A than the other wines, while 'Cabernet Sauvignon' wine contained the highest levels of Vitisin B and Catechin adduct. Vinylphenol adduct only detected in 'conquistador' wine. Generally, the proportions of pyranoanthocyanins in the wines decreased in the order: 'Cabernet Sauvignon' (9.29%) > 'NW196' (3.10%) > 'Moldova' (1.61%) > 'Marselan' (0.74%) > 'Conquistador' (0.05%).

4 Conclusions

In this study, large differences were found in both concentration and composition of the wine anthocyanins of nine varieties. 'Cabernet Sauvignon' and 'Marselan' were characterized by the monoglucoside and pyranoanthocyanins. However, other species were dominated by anthocyanidin 3,5-*O*-diglucosides. 'Yeniang No.2' had the highest acid and total anthocyanin concentration. In the colorimetric analysis, 'Yeniang No.2' wine showed the intensest pigmentation, followed by 'NW196'. 3',4',5'-substituted anthocyanins were dominant in the wines of all varieties, except 'Noble' wine. 'Yeniang No.2' wine had a higher proportion and concentration of coumaroylated anthocyanins. The detected chromatic characteristics of the wines were basically in accordance with their sensory evaluation. These results will not only provide some new insights and stimulate interest in the anthocyanin and color characteristics of wines in different *Vitis* germplasms from southern China, but also be helpful for making use of these varieties and exploiting their quality potential in winemaking.

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Appendix A. The supplementary tables.

Table S1. Data of plant materials from nine different wine grape varieties in southern China.

	V. vinifera		*V. vinifera*× *V. labrusca*	*V. labrusca*		*V. quinquangularis*	*V. quinquangularis*× *V. vinifera*	*V. davidii*	*V. rotundifolia*
	Cabernet Sauvignon	Marselan	Moldova	Conquistador	Saint-Croix	Yeniang No.2	NW196	Xiangniang No.1	Noble
Age of vines	8	3	3	3	3	5	10	3	3
Training system	vertical shoot position	vertical shoot position	vertical shoot position	V shaped frame	V shaped frame	canopy frame	V shaped frame	canopy frame	canopy frame
Irrigation method	drip	drip	drip	drip	drip	drip	drip	drip	drip

Table S2. Chemical characteristics of grape berries from nine varieties[a].

	V. vinifera		*V. vinifera*×*V. labrusca*	*V. labrusca*		*V. quinquangularis*	*V. quinquangularis*× *V. vinifera*	*V. davidii*	*V. rotundifolia*
	Cabernet Sauvignon	Marselan	Moldova	Conquistador	Saint-Croix	Yeniang No.2	NW196	Xiangniang No.1	Noble
Soluble solids (°Brix)	19.00 ± 0.81c	23.83 ± 0.27a	17.30 ± 0.15d	15.00 ± 0.10e	14.50 ± 0.34e	10.00 ± 0.19g	20.00 ± 0.02b	11.50 ± 0.04f	15.00 ± 0.14e
Total acidity (g/L)	9.87 ± 0.66c	7.38 ± 0.27e	10.00 ± 0.26c	4.85 ± 0.04f	8.27 ± 0.16d	37.82 ± 0.71a	11.00 ± 0.10b	2.41 ± 0.03h	3.56 ± 0.14g

[a] Grape data were collected at harvest stage in 2015. Data represent mean±standard error (n =3). In each row, mean values followed by different letters are significantly different ($p < 0.05$).

Table S3. Chemical measures for wines[a].

	V. vinifera		*V. vinifera*× *V. labrusca*	*V. labrusca*		*V. quinquangularis*	*V. quinquangularis*× *V. vinifera*	*V. davidii*	*V. rotundifolia*
	Cabernet Sauvignon	Marselan	Moldova	Conquistador	Saint-Croix	Yeniang No.2	NW196	Xiangniang No.1	Noble
Alcohol (% V/V)	13.30 ± 0.30a	13.10 ± 0.28a	12.10 ± 0.18b	10.80 ± 0.23c	10.50 ± 0.44c	12.20 ± 0.17b	12.10 ± 0.22b	10.30 ± 0.19c	11.90 ± 0.08b
Residual Sugars (g /L)	1.73 ± 0.04e	2.53 ± 0.01d	3.53 ± 0.02a	2.05 ± 0.28e	1.50 ± 0.21g	2.83 ± 0.07c	3.30 ± 0.07b	1.18 ± 0.11g	1.70 ± 0.14f
Titratable Acidity (g /L)	4.82 ± 0.08d	4.56 ± 0.04d	4.43 ± 0.06d	5.68 ± 0.08c	3.90 ± 0.16e	14.23 ± 0.03a	8.33 ± 0.00b	4.52 ± 0.02d	4.51 ± 0.02d
Volatile Acidity (g /L)	0.33 ± 0.01c	0.05 ± 0.00e	0.01 ± 0.00f	0.44 ± 0.01b	0.60 ± 0.00a	0.32 ± 0.02c	0.33 ± 0.01c	0.24 ± 0.00d	0.26 ± 0.01d
pH	3.89 ± 0.07a	2.96 ± 0.01c	4.12 ± 0.01a	3.62 ± 0.02b	3.94 ± 0.03a	3.11 ± 0.03c	3.66 ± 0.05b	3.52 ± 0.04b	3.31 ± 0.02c

[a] Wine data were collected at the end of alcoholic fermentation. Data represent mean±standard error (n =3). In each row, mean values followed by different letters are significantly different ($p < 0.05$).