


# The influence of different pretreatment methods on the quality of wines made from table grapes

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### ABSTRACT

Measurement of phenolics, colour parameters, and volatile compounds in wines were made from two varieties of table grapes ('Zaoheibao' and 'Summer Black') using five pretreatment methods (cold maceration, freezing grapes, lower maturity, fermenting grape juice without skin, and adding tartaric acid) and a control treatment. The effect of the pretreatment methods on the quality of wines was assessed using oenological parameters analysis and volatile compounds analysis. The results indicated that the freezing grape and cold maceration pretreatments improved the colour and increased the contents of phenolic and volatile compounds compared with the control, and freezing was considered to be the most suitable pretreatment method for 'Zaoheibao' wine. With respect to 'Summer Black' wines, cold maceration and lower maturity were considered to be suitable. Cold maceration enhanced the contents of phenolic and volatile compounds, while lower maturity increased the contents of volatile compounds and total acid. Our results provide new insights into the use of table grapes to make different styles of wine.

### KEYWORDS

Zaoheibao, Summer Black, wine, pretreatment methods, HS-SPME-GC-MS

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## 1. INTRODUCTION

Grapes are popular worldwide due to their good palatability, desirable flavour richness and significant economic importance. Global market and trade data released by the U.S. Department of Agriculture show that the world's fresh table grape production have been rise to 27.4 million in 2022, including 12.6 million tons in China, making it the world's largest producer of table grapes. The impact of COVID-19 on international trade has resulted in the supply of table grapes exceeding demand. In order to reduce losses and improve the added value of table grapes, they are processed into juice, dried fruit, fruit wines, and other by-products (Huang et al., 2022). Among these, wine can greatly increase the economic value of table grapes.

The Shanxi Academy of Agricultural Sciences in China bred the grape variety named as 'Zaoheibao', which is well-liked by consumers for its early ripening, large berry, and rich rosé-scented juice (Duan et al., 2020). 'Summer Black' is an early-maturing, seedless, dark purple-black grape cultivar that is widely planted in China and is favoured by the majority of consumers due to its excellent flavour (Jin et al., 2016). Physicochemical properties, colour, polyphenol monomers, and volatile aroma compounds are all significant determinants of wine quality. Wine experts judge a wine's quality based on its sensory qualities (such as aroma, in-mouth properties, or colour), which are impacted by its genetic background, level of maturity, and environmental factors (Sáenz-Navajas et al., 2016).

Furthermore, grape ripening is a critical period that affects the grape composition of compounds in the grapes. The grapes undergo physical (weight, volume, rigidity, and colour) and chemical (pH, acidity, sugars, phenolics, and volatile composition) changes that give them their varietal character (Coelho et al., 2007). During the winemaking process, pretreatment techniques such as freezing increase the volume of intracellular fluid, disrupting cell membranes and providing an easy outlet for the release and solubilisation of anthocyanins and other compounds (Moreno-Perez et al., 2013). Most of the aroma components usually accumulate during cold maceration, while the phenolic and flavour components dissolve and diffuse from the skins and seeds into the must (Casassa et al., 2016). In addition, our past studies have shown that Chenin Blanc from cold maceration contained higher levels of terpenes and esters (Wang et al., 2016).

The main objective of this study was to evaluate the effect of five different pretreatment techniques on the quality of two different varieties of ('Zaoheibao' and 'Summer Black'). These pretreatment techniques for table grapes included cold soaking, freezing, reducing maturity, squeezing juice and adding tartaric acid. This study provides a theoretical basis for the pretreatment of wines from table grapes and will help oenologists to assess the quality of the two varieties.

## 2. MATERIALS AND METHODS

The experiment was carried out using 'Zaoheibao' and 'Summer Black' grapes harvested in 2020.

### 2.1. Chemicals

Folin–Ciocalteu's phenol reagent, gallic acid, and rutin were purchased from Sigma Aldrich (Shanghai, China). The proanthocyanidins (PA) used as a reference, came from Tianjin Jianfeng



Natural Product R&D Co., Ltd (Tianjin, China). All other reagents were analytical grade reagents to be used without further purification.

## 2.2. Vinification

The grapes used were harvested from a vineyard in Tai Gu, Shan Xi Province, China (37.42N, 112.53E). All grapes were of ideal maturity for winemaking (the soluble solids content of ‘Zaoheibao’ was 22 °Brix and ‘Summer Black’ was 25 °Brix), except for the experimental group of grapes with low maturity. The fresh grapes were picked and transported to the laboratory within a couple of hours. All experiments were carried out in triplicate using 10 L fermentation tanks. The pre-treated musts were inoculated with 20 mg L<sup>-1</sup> pectolytic enzymes (Novozymes, Tianjin, China) and 25 g/100 kg Excellence XR *Saccharomyces cerevisiae* (Lamothe-Abiet, Bordeaux, France) and then incubated at 20 °C. Fermentation activity was monitored by estimating CO<sub>2</sub> production through weight loss, and clarifying agent was added at the end of alcoholic fermentation. For all experiments, fermentation kinetics were the same after 10 days, and the end of fermentation was confirmed by measuring reducing sugars. At the end of fermentation, the wine was treated with a 30 mg L<sup>-1</sup> solution of SO<sub>2</sub> and cold stabilised (-4 °C) for 2 weeks before being analysed.

The control group and five pretreatment groups were as follows:

- a) No pretreatment, control (CK): the grapes were destemmed directly, crushed, and then fermented in 10 L fermentation tanks (‘Zaoheibao’ is noted as ZCK, ‘Summer Black’ as SCK).
- b) Freezing grapes (FG): grapes were frozen at -20 °C for 24 h prior crushing (ZFG, SFG).
- c) Cold maceration (CM): cold maceration of the must at -4 °C for 48 h (ZCM, SCM)
- d) Grapes of lower maturity (BM): ‘Zaoheibao’ and ‘Summer Black’ grapes harvested before reaching industrial maturity, with a total soluble solids content of 18 °Brix and 22 °Brix, respectively (ZBM, SBM).
- e) Added tartaric acid (AT): tartaric acid was added to the must at a concentration of 0.85 g L<sup>-1</sup> (ZAT, SAT).
- f) Only juice (OM): the juice was obtained by pressing the grapes and the pressed juice was fermented in a 10 L fermentation tank (ZOM, SOM).

## 2.3. Oenological parameters’ analysis

The ethanol content (OIV-MA-AS312-01), total acidity (OIV-MA-AS313-01), volatile acidity (OIV-MA-AS313-02), and reducing sugar contents (OIV-MA-AS311-01A) of wines were determined according to OIV analytical methods. The content of total phenolics in wine was determined according to the Folin–Ciocalteu colorimetric method expressed as gallic acid equivalent (Deng et al., 2011). The absorbance was measured at 765 nm. Total flavanols were measured at 510 nm using the method described by Kim et al. (2003), and the results were expressed as catechin equivalents. The total anthocyanins were measured using the pH differential method described by Boyles and Wrolstad (1993), expressed as mg Mvd-3-Glu equivalents. Total tannins (mg L<sup>-1</sup> (+)-catechin) were measured as previously described by Rajkovic and Sredović Ignjatović (2009). The chromatic properties in the CIELAB space were measured by the method of Haria (Benucci, 2020). All determinations were performed in triplicate, the results are expressed as means ± S.D.



## 2.4. Volatile compounds analysis

The volatile compounds were extracted by headspace solid-phase microextraction using a 2 cm, 50/30  $\mu\text{m}$  DVB/CAR/PDMS fibre (Supelco, Bellefonte, PA, USA) and analysed using gas chromatography-mass spectrometry (GC-MS). 8 mL wine samples, 2.4 g NaCl, and 10  $\mu\text{L}$  2-octanol (internal standard) were held in the 20 mL headspace bottle, which was stirred and equilibrated by a magnetic bar in a 45 °C water bath for 10 min. After that, the fibre was exposed to the wine headspace for 30 min at 45 °C immediately followed by thermo-desorption of the fibre in the GC-injector for 5 min (Li et al., 2007). TRACE DSQ (Thermo-Finnigan, USA) with a TR5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ , Thermo-Finnigan, USA) was used for GC-MS analysis. The temperature program for GC-MS analysis was as follows: initial temperature of 40 °C was maintained for 3 min, then increased to 130 °C at 3 °C  $\text{min}^{-1}$ , and then to 230 °C at 4 °C  $\text{min}^{-1}$  for 2 min. The mass spectrometer was operated in scan mode in the range of 29–350 amu, and the ion source and transfer line temperature was 250 °C (Tao et al., 2008). The volatile compounds were identified and quantified by comparing the retention times and mass spectra in the NIST2.0 MS library. The concentrations of the major aroma compounds were calculated using the relative area relative to the internal standard 2-octanol.

## 2.5. Statistical analysis

One-way analysis of variance (ANOVA) was completed by SPSS 22.0 software and the Duncan test was used for multiple mean comparisons. Relative concentration differences of volatile compounds between treatments and control were calculated and presented as average per compound group in heatmaps. OriginPro2021 software was used to create graphs.

# 3. RESULTS AND DISCUSSION

## 3.1. Basic chemical composition and phenolic compounds

Table 1 lists the ethanol content, total acidity, and phenolic compounds of wines fermented using different pretreatment methods. The ethanol content of ‘Summer Black’ wine was significantly higher than that of ‘Zaoheibao’, while that of BM (ZBM and SBM) was significantly lower than that of other groups ( $P < 0.05$ ). In addition, the total acidity of the ‘Summer Black’ was significantly higher than that of the ‘Zaoheibao’ ( $P < 0.05$ ).

In terms of phenolic compounds, the ‘Summer Black’ wine contained higher levels of total phenolics, tannins, anthocyanins, and flavonoids than the ‘Zaoheibao’ wine in non-pretreatment fermentation. Though different pretreatment technologies, both CM and FG had significantly higher levels of total phenolics, tannins, anthocyanins, and flavonoids than CK ( $P < 0.05$ ), with ZFG and SCM having the highest levels. Maceration and fermentation time in contact with the skins and seeds of wines, pressing, maturation, clarification, and bottle ageing were all factors influencing the phenolic composition of wines (Paixao et al., 2007). Tannins provide astringency to wines, an important aspect of organoleptic quality, and are mainly responsible for the dryness, roughness, and pucker of wines. The cold maceration pretreatment increased the total phenolic and tannin contents of the wines compared to the control. In addition, the freezing pretreatment should also produce wines with higher polyphenols content as they can be easily extracted from the skins of the grapes (Gordillo et al., 2010). On the contrary, the contents of total phenolic,



Table 1. Chemical composition in wines produced with five pretreatments

Pretreatment	Ethanol (% vol)	Total acidity (g L <sup>-1</sup> )	Total phenolic (mg L <sup>-1</sup> )	Total tannin (mg L <sup>-1</sup> )	Total anthocyanin (mg L <sup>-1</sup> )	Total flavonoid (mg L <sup>-1</sup> )
ZCK	11.23 ± 0.21d	5.19 ± 0.07bc	745.12 ± 20.63c	45.18 ± 2.06b	42.86 ± 2.35b	443.35 ± 23.06c
ZBM	9.70 ± 0.20e	5.21 ± 0.02abc	717.44 ± 4.68d	31.42 ± 1.12c	23.53 ± 1.76c	307.47 ± 19.21d
ZOM	12.31 ± 0.15b	5.25 ± 0.05ab	360.26 ± 0.11f	18.83 ± 1.43d	11.45 ± 0.80d	147.67 ± 14.90e
ZFG	12.60 ± 0.10a	5.15 ± 0.02d	1051.54 ± 22.88a	63.10 ± 1.57a	45.73 ± 0.95a	636.39 ± 32.31a
ZCM	11.83 ± 0.15c	5.12 ± 0.02d	826.66 ± 24.84b	61.76 ± 2.43a	45.94 ± 1.27a	545.17 ± 25.42b
ZAT	11.40 ± 0.20d	5.26 ± 0.02a	660.00 ± 22.43e	44.71 ± 1.92b	44.25 ± 0.72ab	415.42 ± 18.50c
SCK	13.30 ± 0.26b	6.46 ± 0.02d	1098.72 ± 32.60c	82.70 ± 4.10c	131.28 ± 2.34d	649.28 ± 21.94c
SBM	11.70 ± 0.30d	6.74 ± 0.02c	1003.59 ± 26.67d	61.70 ± 7.02d	84.19 ± 2.22e	586.87 ± 13.94d
SOM	13.70 ± 0.10a	6.79 ± 0.01b	567.69 ± 10.61e	31.90 ± 1.59e	57.07 ± 1.35f	316.03 ± 7.51e
SFG	12.76 ± 0.12c	6.42 ± 0.01e	1274.35 ± 22.74b	88.95 ± 1.79b	168.06 ± 2.56b	798.80 ± 18.12b
SCM	13.00 ± 0.15bc	6.39 ± 0.01f	1420.51 ± 66.15a	95.33 ± 2.68a	177.15 ± 2.03a	886.76 ± 32.35a
SAT	13.13 ± 0.06b	6.83 ± 0.02a	1037.95 ± 14.27d	81.56 ± 0.53c	146.28 ± 2.23c	590.73 ± 17.13d

Values are expressed as mean ± SD ( $n = 3$ ). Different letters in each column indicate significant differences according to the Duncan test ( $P < 0.05$ ).



tannin, anthocyanin, and flavonoid in BM and OM (including ZBM, ZOM, SBM, and SOM) wines decreased significantly ( $P < 0.05$ ). This result proves that phenolic compounds in grapes are related to the degree of maturation and are mainly present in the skins and seeds, with lower levels in the pulp (Harbertson et al., 2002).

Overall, the content of ethanol, total acidity, and phenolic compounds was higher in the ‘Summer Black’ wines than in the ‘Zaoheibao’ wines. With respect to pretreatment technologies, although cold maceration and freezing significantly increased the phenolic compounds content ( $P < 0.05$ ) and decreased the total acidity, freezing was the most suitable pretreatment for the ‘Zaoheibao’, while cold maceration was more suitable for the ‘Summer Black’ wine.

### 3.2. Colour parameters

The  $a^*$  and  $b^*$  of the ‘Zaoheibao’ were significantly lower than those of the ‘Summer Black’ wine (Fig. 1). The different pretreatments in wine production affected the colour parameters, especially the red ( $a^*$ ) and yellow ( $b^*$ ) coordinators. ZCM and SFG wine had higher  $a^*$  values than CK, while ZOM and SOM had the lowest  $a^*$  values due to the lack of skin contact. CM (ZCM and SCM) wine had higher  $b^*$  values, meaning a higher proportion of yellow, while OM (ZOM and SOM) had the lowest  $b^*$  values. It has been reported that the value of  $a^*$  is positively correlated with anthocyanins (Lago-Vanzela et al., 2014). The results indicated that freezing and cold maceration pretreatment resulted in higher yellow and red colours in the wines, and the ‘Summer Black’ grapes contained more anthocyanins than the ‘Zaoheibao’ grapes.

### 3.3. Volatile compounds

The formation of wine aromas is the result of a delicate balance of multiple volatile compounds. The concentrations of volatile compounds identified and quantified from the wine samples of the two varieties are shown in Table 2. Also, the correlation and separation of volatile compounds and different pretreatments in the wines were revealed by principal component analysis (PCA) (Fig. 2). Figure 2 and Table 2 show the significantly higher content of aroma compounds in the BM, FG, and CM groups in the ‘Zaoheibao’ and ‘Summer Black’ wine samples.

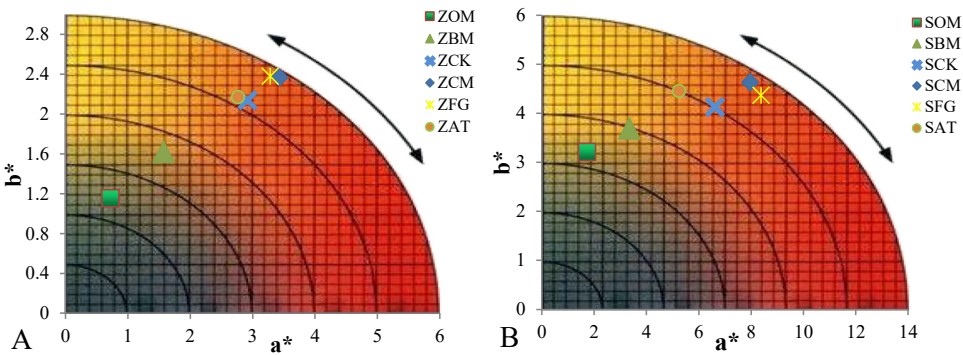


Fig. 1. Corresponding CIELAB coordinates of pretreated wines from ‘Zaoheibao’ (A) and ‘Summer Black’ (B) grapes



Table 2. Content of volatile compounds in different pretreated wines

Compound	'Zaoheibao'					'Summer Black'						
	C ( $\mu\text{g L}^{-1}$ ) ZCK	C ( $\mu\text{g L}^{-1}$ ) ZBM	C ( $\mu\text{g L}^{-1}$ ) ZOM	C ( $\mu\text{g L}^{-1}$ ) ZFG	C ( $\mu\text{g L}^{-1}$ ) ZCM	C ( $\mu\text{g L}^{-1}$ ) ZAT	C ( $\mu\text{g L}^{-1}$ ) SCK	C ( $\mu\text{g L}^{-1}$ ) SBM	C ( $\mu\text{g L}^{-1}$ ) SOM	C ( $\mu\text{g L}^{-1}$ ) SFG	C ( $\mu\text{g L}^{-1}$ ) SCM	C ( $\mu\text{g L}^{-1}$ ) SAT
1-Hexanol	31.87 $\pm$ 1.86 <sup>b</sup>	25.47 $\pm$ 2.57 <sup>c</sup>	0 <sup>d</sup>	41.49 $\pm$ 1.72 <sup>a</sup>	31.47 $\pm$ 1.91 <sup>b</sup>	23.95 $\pm$ 1.89 <sup>e</sup>	26.63 $\pm$ 3.75 <sup>d</sup>	46.51 $\pm$ 9.69 <sup>c</sup>	65.80 $\pm$ 5.14 <sup>b</sup>	109.24 $\pm$ 11.80 <sup>a</sup>	30.56 $\pm$ 2.23 <sup>d</sup>	42.89 $\pm$ 0.69 <sup>f</sup>
2-Phenylethanol	189.52 $\pm$ 16.86 <sup>a</sup>	92.24 $\pm$ 11.62 <sup>c</sup>	122.37 $\pm$ 11.14 <sup>b</sup>	123.24 $\pm$ 10.65 <sup>b</sup>	117.69 $\pm$ 10.07 <sup>b</sup>	68.63 $\pm$ 2.74 <sup>d</sup>	298.33 $\pm$ 25.60 <sup>c</sup>	<u>605.79</u> $\pm$ <u>39.02</u> <sup>a</sup>	177.41 $\pm$ 12.79 <sup>e</sup>	210.77 $\pm$ 19.05 <sup>de</sup>	221.92 $\pm$ 17.06 <sup>d</sup>	378.90 $\pm$ 24.96 <sup>b</sup>
Isoamyl acetate	138.79 $\pm$ 13.63 <sup>c</sup>	861.73 $\pm$ 49.25 <sup>a</sup>	280.39 $\pm$ 7.56 <sup>c</sup>	222.88 $\pm$ 9.46 <sup>d</sup>	328.28 $\pm$ 10.35 <sup>b</sup>	93.37 $\pm$ 4.42 <sup>f</sup>	526.90 $\pm$ 35.80 <sup>c</sup>	<u>689.68</u> $\pm$ <u>54.18</u> <sup>b</sup>	371.85 $\pm$ 19.26 <sup>d</sup>	514.08 $\pm$ 33.09 <sup>e</sup>	1216.66 $\pm$ 78.74 <sup>a</sup>	379.19 $\pm$ 31.24 <sup>d</sup>
Ethyl hexanoate	50.94 $\pm$ 2.64 <sup>e</sup>	<u>201.07</u> $\pm$ <u>6.85</u> <sup>a</sup>	88.54 $\pm$ 7.23 <sup>c</sup>	<u>69.38</u> $\pm$ <u>6.03</u> <sup>i</sup>	<u>105.26</u> $\pm$ <u>15.87</u> <sup>b</sup>	35.38 $\pm$ 8.02 <sup>f</sup>	96.82 $\pm$ 11.02 <sup>c</sup>	<u>267.20</u> $\pm$ <u>24.86</u> <sup>b</sup>	105.52 $\pm$ 13.61 <sup>e</sup>	<u>179.78</u> $\pm$ <u>21.96</u> <sup>b</sup>	<u>247.69</u> $\pm$ <u>27.28</u> <sup>a</sup>	103.89 $\pm$ 21.47 <sup>e</sup>
Hexyl acetate	nd	nd	nd	nd	nd	nd	22.94 $\pm$ 5.42 <sup>b</sup>	29.44 $\pm$ 4.83 <sup>b</sup>	20.28 $\pm$ 3.18 <sup>b</sup>	28.58 $\pm$ 3.01 <sup>b</sup>	<u>55.38</u> $\pm$ <u>9.10</u> <sup>a</sup>	14.96 $\pm$ 1.65 <sup>e</sup>
2-Phenylethyl	nd	nd	nd	nd	nd	nd	30.50 $\pm$ 0.10 <sup>e</sup>	21.97 $\pm$ 1.06 <sup>c</sup>	25.79 $\pm$ 3.23 <sup>b</sup>	25.62 $\pm$ 2.53 <sup>b</sup>	12.70 $\pm$ 2.09 <sup>d</sup>	33.57 $\pm$ 1.10 <sup>a</sup>
Phenylacetate												
Ethyl octanoate	85.96 $\pm$ 8.86 <sup>d</sup>	537.90 $\pm$ 12.58 <sup>a</sup>	215.09 $\pm$ 16.53 <sup>b</sup>	<u>155.12</u> $\pm$ <u>14.36</u> <sup>c</sup>	<u>229.39</u> $\pm$ <u>10.82</u> <sup>b</sup>	88.93 $\pm$ 7.67 <sup>d</sup>	176.10 $\pm$ 15.46 <sup>c</sup>	481.75 $\pm$ 32.94 <sup>a</sup>	198.57 $\pm$ 16.48 <sup>e</sup>	<u>373.51</u> $\pm$ <u>20.60</u> <sup>b</sup>	<u>482.96</u> $\pm$ <u>34.15</u> <sup>a</sup>	190.39 $\pm$ 24.16 <sup>e</sup>
Ethyl decanoate	24.60 $\pm$ 6.96 <sup>c</sup>	<u>108.53</u> $\pm$ <u>2.14</u> <sup>a</sup>	34.65 $\pm$ 3.82 <sup>c</sup>	<u>71.41</u> $\pm$ <u>5.80</u> <sup>b</sup>	<u>63.24</u> $\pm$ <u>9.64</u> <sup>a</sup>	34.93 $\pm$ 1.82 <sup>c</sup>	21.49 $\pm$ 2.03 <sup>de</sup>	<u>69.25</u> $\pm$ <u>3.39</u> <sup>b</sup>	29.79 $\pm$ 1.41 <sup>d</sup>	<u>94.87</u> $\pm$ <u>7.92</u> <sup>a</sup>	<u>55.25</u> $\pm$ <u>7.86</u> <sup>c</sup>	19.53 $\pm$ 1.35 <sup>e</sup>
Ethyl dodecanoate	20.54 $\pm$ 4.49 <sup>b</sup>	13.65 $\pm$ 2.51 <sup>c</sup>	11.89 $\pm$ 1.41 <sup>c</sup>	<u>36.37</u> $\pm$ <u>2.56</u> <sup>a</sup>	14.53 $\pm$ 0.29 <sup>e</sup>	23.67 $\pm$ 2.33 <sup>b</sup>	14.99 $\pm$ 1.76 <sup>e</sup>	<u>36.33</u> $\pm$ <u>2.79</u> <sup>b</sup>	20.26 $\pm$ 1.43 <sup>d</sup>	<u>50.87</u> $\pm$ <u>5.82</u> <sup>a</sup>	<u>47.79</u> $\pm$ <u>6.38</u> <sup>a</sup>	27.38 $\pm$ 2.01 <sup>c</sup>
Ethyl salicylate	nd	nd	nd	nd	nd	nd	10.97 $\pm$ 0.41 <sup>de</sup>	<u>34.88</u> $\pm$ <u>1.23</u> <sup>a</sup>	9.21 $\pm$ 0.98 <sup>c</sup>	<u>28.73</u> $\pm$ <u>2.53</u> <sup>b</sup>	11.76 $\pm$ 1.07 <sup>d</sup>	25.71 $\pm$ 0.30 <sup>e</sup>
Phenethyl acetate	74.53 $\pm$ 8.27 <sup>c</sup>	<u>143.81</u> $\pm$ <u>14.79</u> <sup>a</sup>	101.03 $\pm$ 1.51 <sup>b</sup>	61.04 $\pm$ 11.30 <sup>c</sup>	76.76 $\pm$ 10.87 <sup>c</sup>	41.41 $\pm$ 1.56 <sup>d</sup>	187.48 $\pm$ 15.01 <sup>c</sup>	<u>284.38</u> $\pm$ <u>15.30</u> <sup>a</sup>	252.61 $\pm$ 12.31 <sup>b</sup>	<u>101.73</u> $\pm$ <u>8.89</u> <sup>c</sup>	195.13 $\pm$ 13.18 <sup>c</sup>	136.84 $\pm$ 2.88 <sup>d</sup>
Linalool	88.97 $\pm$ 6.93 <sup>bc</sup>	35.33 $\pm$ 4.52 <sup>d</sup>	76.73 $\pm$ 9.92 <sup>c</sup>	<u>139.04</u> $\pm$ <u>17.24</u> <sup>a</sup>	<u>138.91</u> $\pm$ <u>10.42</u> <sup>a</sup>	102.73 $\pm$ 14.80 <sup>b</sup>	nd	nd	nd	nd	nd	nd
Rosenoxide	18.87 $\pm$ 2.19 <sup>c</sup>	13.70 $\pm$ 1.52 <sup>cd</sup>	7.60 $\pm$ 1.51 <sup>d</sup>	<u>28.80</u> $\pm$ <u>8.09</u> <sup>a</sup>	<u>26.01</u> $\pm$ <u>0.55</u> <sup>ab</sup>	19.90 $\pm$ 2.05 <sup>b</sup>	10.62 $\pm$ 2.13 <sup>d</sup>	<u>31.98</u> $\pm$ <u>2.44</u> <sup>b</sup>	38.74 $\pm$ 6.05 <sup>a</sup>	<u>18.88</u> $\pm$ <u>2.28</u> <sup>c</sup>	<u>15.43</u> $\pm$ <u>2.01</u> <sup>c</sup>	12.61 $\pm$ 0.86 <sup>d</sup>
$\alpha$ -Terpineol	29.89 $\pm$ 5.24 <sup>b</sup>	26.89 $\pm$ 1.94 <sup>b</sup>	0.00 <sup>f</sup>	29.18 $\pm$ 3.20 <sup>b</sup>	29.80 $\pm$ 1.68 <sup>b</sup>	36.36 $\pm$ 3.32 <sup>a</sup>	nd	nd	nd	nd	nd	nd
Citronellol	185.45 $\pm$ 24.20 <sup>b</sup>	79.79 $\pm$ 8.94 <sup>d</sup>	25.08 $\pm$ 2.57 <sup>c</sup>	<u>213.70</u> $\pm$ <u>4.69</u> <sup>a</sup>	182.86 $\pm$ 18.06 <sup>b</sup>	165.31 $\pm$ 10.73 <sup>b</sup>	76.90 $\pm$ 14.89 <sup>a</sup>	91.74 $\pm$ 10.62 <sup>a</sup>	55.13 $\pm$ 6.82 <sup>b</sup>	86.47 $\pm$ 11.05 <sup>a</sup>	48.29 $\pm$ 7.11 <sup>b</sup>	95.93 $\pm$ 12.26 <sup>a</sup>
Geraniol	35.46 $\pm$ 1.13 <sup>b</sup>	27.42 $\pm$ 2.72 <sup>c</sup>	18.79 $\pm$ 1.08 <sup>d</sup>	<u>55.45</u> $\pm$ <u>11.09</u> <sup>a</sup>	35.82 $\pm$ 3.18 <sup>b</sup>	52.03 $\pm$ 1.56 <sup>b</sup>	nd	nd	nd	nd	nd	nd
Damascenone	15.26 $\pm$ 2.41 <sup>c</sup>	20.13 $\pm$ 2.47 <sup>b</sup>	17.93 $\pm$ 1.27 <sup>bc</sup>	<u>25.81</u> $\pm$ <u>1.87</u> <sup>a</sup>	17.66 $\pm$ 0.27 <sup>bc</sup>	16.97 $\pm$ 3.19 <sup>b</sup>	11.61 $\pm$ 0.91 <sup>b</sup>	<u>14.27</u> $\pm$ <u>1.56</u> <sup>a</sup>	12.44 $\pm$ 1.23 <sup>ab</sup>	13.88 $\pm$ 0.53 <sup>a</sup>	13.36 $\pm$ 0.80 <sup>a</sup>	13.16 $\pm$ 0.42 <sup>a</sup>
Butylated hydroxytoluene	29.82 $\pm$ 0.14 <sup>c</sup>	<u>55.47</u> $\pm$ <u>3.87</u> <sup>a</sup>	15.74 $\pm$ 0.68 <sup>d</sup>	31.20 $\pm$ 1.98 <sup>c</sup>	<u>39.39</u> $\pm$ <u>2.41</u> <sup>b</sup>	26.06 $\pm$ 5.25 <sup>e</sup>	59.73 $\pm$ 2.75 <sup>b</sup>	<u>79.82</u> $\pm$ <u>8.14</u> <sup>a</sup>	35.50 $\pm$ 1.22 <sup>c</sup>	39.72 $\pm$ 2.21 <sup>c</sup>	60.51 $\pm$ 6.57 <sup>b</sup>	32.51 $\pm$ 5.64 <sup>c</sup>

Data show average of triplicates  $\pm$ SD. Different letters within rows indicate differences among wine treatments determined by the Duncan test at 95% confidence. "nd": the compound was not detected by GC-MS in the corresponding wine sample. Underlined are values that highlight significant increases compared to the control group.



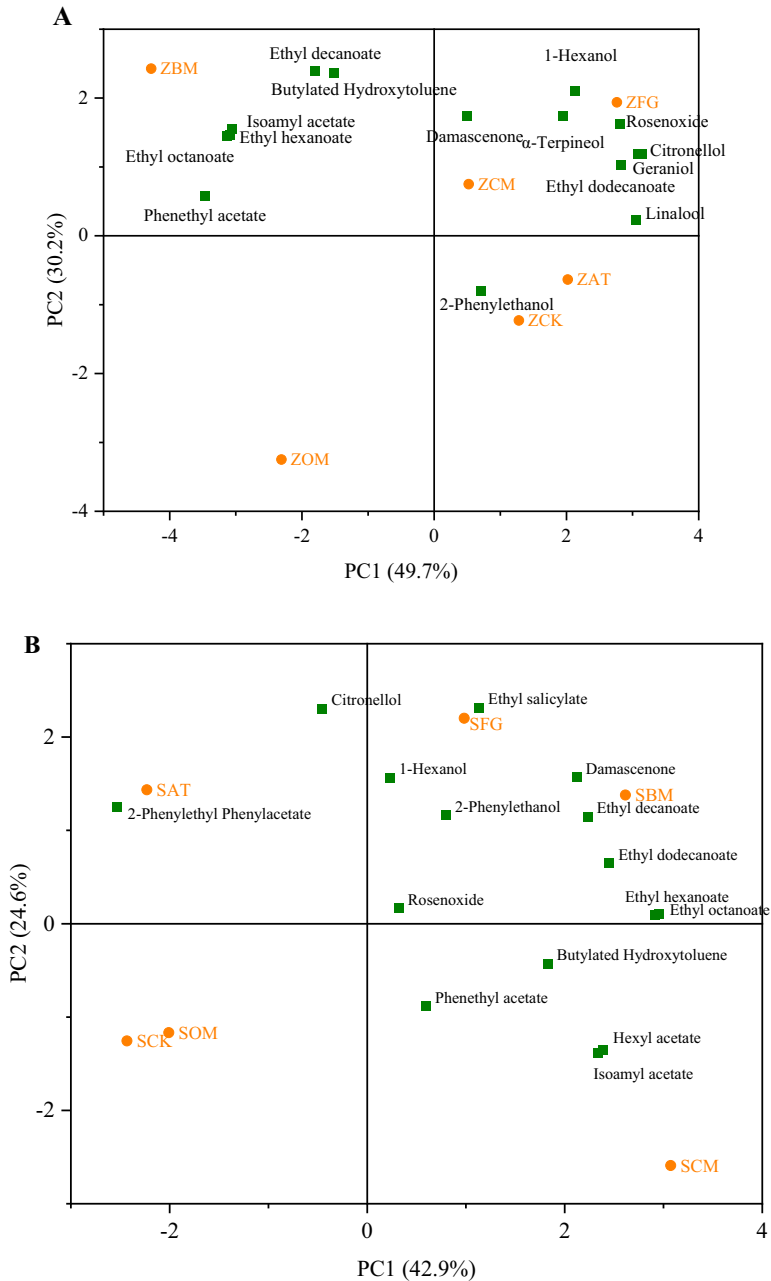


Fig. 2. Principal component analysis of volatile compounds in 'Zaoheibao' wines (A) and 'Summer Black' (B) wines made with different pretreatments. ●: Wine samples; ■: Volatile compounds





As far as ‘Zaoheibao’ is concerned, the different pretreatment technologies mainly affected the content of esters and terpenes (Table 2). PCA result shows that 79.9% of the variance is explained by the 15 different volatile compounds in the ‘Zaoheibao’ wine (Fig. 2A). ZBM, ZCM, and ZFG are located in the positive direction of PC2, and most volatile compounds are on this axis. The ZBM wines were more influenced by esters than the other groups, contributing banana, green apple, fatty, floral, and sweet aromas (Peinado et al., 2006; Noguerol-Pato et al., 2012). Unlike ZBM, ZFG was more influenced by terpenes such as linalool, rosenoxide, citronellol, and geraniol than other ‘Zaoheibao’ wines, which had stronger flowery, lychee, citric, wine, and geranium aromas (Peinado et al., 2006; Noguerol-Pato et al., 2012). Therefore, freezing appears to have a more positive effect when considering the increase in volatile compound content and abundance in ‘Zaoheibao’. The Muscat wines produced by freezing also contained more aromatic substances (Ruiz-Rodriguez et al., 2020).

For the ‘Summer Black’ wine, the first two principal components (PCs) explained 67.5% of the total variance, as shown in Fig. 2B. SCM wine is located in the lower right quadrant, where isoamyl acetate and hexyl acetate are also clustered, contributing to the fruit (banana, apple, pear, etc.) and flower characteristic aromas of the SCM wine samples (Peinado et al., 2006). It is noteworthy that both SFG and SBM are located in the upper right quadrant but farther apart. SFG offered with more herbal, honey and floral aromas, while SBM provided more fruity (banana, pear, green apple), floral, sweet, and fatty aromatic characteristics (Peinado et al., 2006; Noguerol-Pato et al., 2012). Aith Barbará et al. (2020) similarly concluded that wines made from less mature (19 °Brix) Syrah grapes had a higher content of volatiles with pleasant odour and higher intensity and persistence.

Overall, in terms of volatile compounds, freezing is the appropriate pretreatment for ‘Zaoheibao’ wines, while the appropriate pretreatment for ‘Summer Black’ is to use grapes of lower maturity with the appropriate pretreatment helping to increase or improve the content of the volatile compounds. This conclusion is inconsistent with the results of the phenolic compounds analysis, implying that pretreatment methods have different effects on different compounds and require comprehensive analysis and consideration.

### 3.4. Heatmap visualisation analysis

Heatmaps were applied to visualise the differences and correlation in ethanol, total acidities, phenolic compounds, and volatile compounds in wine samples fermented with different pretreatment methods (Fig. 3). Figure 3A shows that the ZFG and ZCM clustered into a single cluster, clearly differentiated from the other samples in terms of colour intensity, which is consistent with the result of PCA. The orange cells in the ZFG column were more intense and more prominent than in the other samples, meaning higher content of volatile and phenolic compounds, which can improve the quality of ‘Zaoheibao’ wine.

Unlike the ‘Zaoheibao’ wines’ results, the ‘Summer Black’ wines were divided into two large clusters (Fig. 3B). The one cluster comprised the SCK, SAT, and SOM wines, while the another cluster included SBM, SFG, and SCM wines with more orange cells in the columns. Further, SFG and SCM were divided into one subcluster, meaning that these two wines had similar changes in their compounds. 8 volatile compounds and 4 phenolic compounds in the SCM and SFG columns had a darker orange cell than SCK, while SBM wine only had orange cell in 12 volatile compounds and total acid. This implies that ‘Summer Black’ can be pretreated with both cold maceration and lower maturity to produce different styles of wine.



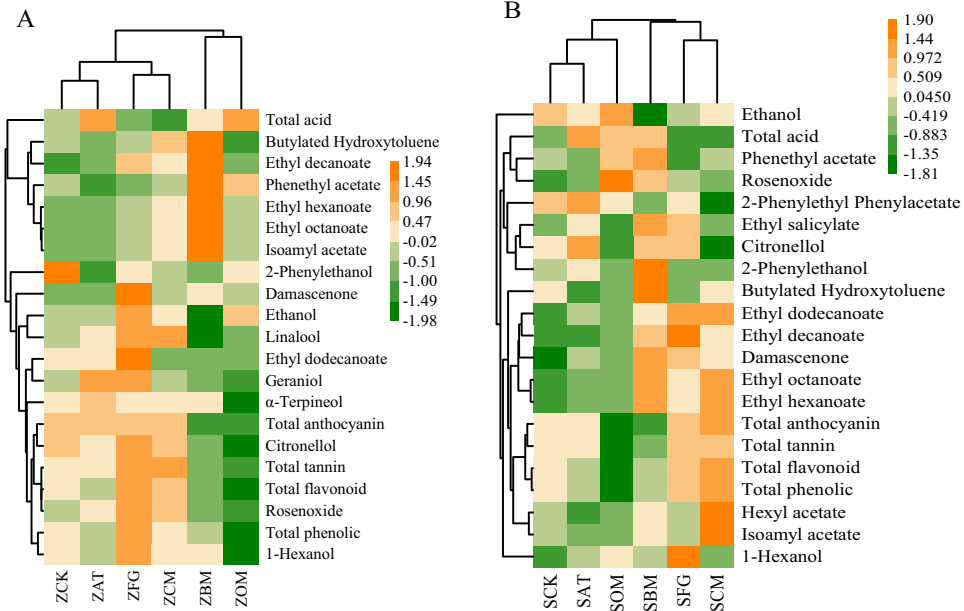


Fig. 3. Heatmap visualisation of ethanol, total acid, phenolic compounds, and volatile compounds contents in ‘Zaoheibao’ (A) and ‘Summer Black’ (B) wines fermented with different pretreatment methods. Relative concentration differences between treatments and control

### 4. CONCLUSIONS

In this research, the effect of pretreatment methods on the quality of ‘Zaoheibao’ and ‘Summer Black’ grape cultivars was evaluated by analysing the physicochemical composition, colour parameters, and volatile compounds of the wines. The results showed that the different pretreatment methods had an obvious impact on the compound content of the wines, and that differences in varietal characteristics also had a significant impact on the compound content of the wines. For the ‘Zaoheibao’ wine, freezing may be the most appropriate pretreatment, which produced a wine with more phenolic compounds, brighter colour, and more flavour compounds. However, for ‘Summer Black’ wines, cold maceration and lower maturity may be relatively good pretreatment methods to produce two different styles of high quality wines. These results not only provided data to support table grape winemaking, but also provided promising insights into improving the quality and enriching the style of the wine and even other fermented wines.

*Conflict of interest:* The authors declare no competing financial interest.

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