



Changes of Volatile Compounds in Table Grapes During Postharvest Storage by SPME Coupled with GC-MS

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Volatile compounds of four table grape cultivars, 'Tengnian', 'Longan', 'Cow's Teat' and 'Emerald non-nuclear' were investigated during postharvest storage by SPME/GC-MS. Using the principal component analysis, relations between volatile compounds were associated with cultivars. The results showed that volatile compounds in the four cultivars of table grapes were different and all changed a lot during postharvest storage. Initially a total of 44 volatile compounds, including alcohols, carbonyls, esters and acids, were found in the four cultivars, while only 25 compounds were detected at the end of storage. In addition, the relevant taste indexes total sugar (^oBrix), total acidity (titratable acidity, TA) and sugar acid ratio in different cultivar of grape berry were also determined. It was possible to discriminate the results to monitor the loss of freshness for table grape during storage.

Key Words: Table grape, Volatile compounds, SPME, GC-MS, Postharvest.

INTRODUCTION

China is the fourth largest producer of grape and is the largest fresh grape consumption market in the world, with more than 65 % of the produced grapes being consumed as table grapes¹. The shelf life of the grape berry is affected by many factors including cultivar, stage of ripeness and storage atmosphere or temperature². As to grapes freshness, many researchers focused on indexes such as nutrition and microorganism^{3,4}. However, for consumers, the major considerations for grapes are the appearance, texture and flavour⁵.

Volatile compounds are main contribution to the quality of grapes⁶. Volatile compounds may even influence taste thresholds, sweetness perception and pleasantness and have been considered to play key roles in food preference and acceptability. Therefore, it is important to maintain flavor substances in grape.

Concentration of volatile compounds depends on grape cultivar, growing regions and climatic or biological factors⁶. Moreover, grape volatile composition can greatly vary during ripening and storage. During the past years, researches focused on the changes of volatile and aroma compounds in different kinds of vinifera, grape juice and wine have become relevant^{7,8}. However, little attention has been focused on the volatile aromas of table grapes⁹.

Volatile compounds embody a challenge by means of quantification and different methods for a practical determination have been proposed¹⁰. The individual analysis of free and bound aromas is quite complex due to their chemical and physical properties, as well as their trace amounts found in grapes, especially in non-aromatic varieties. Volatile compounds of grapes generally require a previous step of isolation and concentration for the subsequent gas chromatography analysis⁶. Solid-phase micro extraction (SPME) is a fast, simple and solvent-free technique. Thanks to the appearance of different types of adsorbents with a wide range of polarity, it is possible to isolate trace compounds of different substrates^{11,12}.

To search efficient preservation methods for keeping table grape flavor during shelf life, this study required to elucidate the changes of main volatile compounds in four popular cultivars of table grape during storage and the effect of taste indexes, such as total sugar (^oBrix), total acidity and sugar acid ratio on volatile compounds. These indexes also influenced consumer preference and acceptability towards table grape flavor to a certain extent.

EXPERIMENTAL

Four table grape cultivars with different flavours, 'Tengnian' (hybrid between *V. vinifera* and *V. labrusca* cultivars, *Vitis labruscana* Kyoho), 'Longan' (*V. vinifera proles orientalis*

Negr.), 'Cow's Teat' (*V. vinifera proles orientalis Negr.*) and 'Emerald non-nuclear' (*V. vinifera proles orientalis Negr.*) were studied. The berries of all the four previous grape cultivars were harvested at commercial maturity in vineyard at Hangzhou (China) suburb and then were immediately transported to the laboratory. The grape were selected on the basis of uniform colour, size, firmness and the absence of blemishes or disease and randomly distributed into batches. There were three replicates per sampling for analyzing the total sugar content ($^{\circ}$ Brix), total acid (titratable acidity, TA) and volatile compound analysis.

Solid phase micro extraction (SPME): Grapes were grounded into pulp, then a 10 mL sample was poured into a 20 mL gas-tight vial containing a microstirring bar (Supelco) to study the effects of extraction time and temperature. Two SPME fiber coatings were evaluated and used-85 μ m polyacrylate (PA), 65 μ m polydimethylsiloxane (PDMS)/divinylbenzene (DVB) (Supelco, Bellefonte PA, USA)-for their high sensitivity for aroma compounds and good reproducibility in grapes^{6,9}. Fibers were first conditioned following instructions from manufacturers then cleaned at 250 $^{\circ}$ C for 10 min. The sample was equilibrated at 50 $^{\circ}$ C for 5 min and extracted by the fiber for 25 min at the same temperature. After extraction, the fiber was withdrawn and introduced into the injector port of the GC for desorption at 250 $^{\circ}$ C for 3 min in the splitless mode. Analyses were carried out in triplicate.

Gas chromatography-mass spectrometry (GC-MS): GC-MS analysis was performed on an Agilent gas chromatograph model 7890 A coupled with an Agilent 5975 C mass selective detector (Agilent Technologies). Analytes were separated on an DB-5 capillary column (0.25 mm \times 30 m \times 1.0 μ m) by applying the following temperature program: 40 $^{\circ}$ C for 5 min, raised to 120 $^{\circ}$ C at 15 $^{\circ}$ C/min and kept for 2 min, then increased to 240 $^{\circ}$ C at 10 $^{\circ}$ C/min and held for 6 min.

The mass detector conditions were: electronic impact (EI) mode at 70 eV; source temperature: 230 $^{\circ}$ C; mass scanning range: m/z 30-450. The flow rate of helium was 1 mL/min. Compounds were identified by comparison with reference spectra (Wiley 5 and NIST 98 databases), which were compared with available literature retention indices (NIST Chemistry Web Book, 2011).

Statistic analysis: The content of each compound identified in grape was determined by area normalization method. The statistical significance of the volatile compounds was determined by one-way ANOVA. The SPME-GC-MS analyses were performed in triplicate. Principal component analysis (PCA) was carried out using SPSS 19.0 software for Windows statistical package. PCA was applied for reducing the number of variables (four variables corresponding to the chemical classes of the individual volatile compounds identified) to a smaller number of new derived variables (principal component or factors) that adequately summarize the original information.

RESULTS AND DISCUSSION

Extracting properties of solid phase microextraction fibers: A standard mixture of analysis commonly found in volatile was used for the preliminary selection of different fibers and extraction methods.

Extraction temperature and time are important parameters in the SPME sampling process and both of which have an effect on the equilibrium during extraction. Extractions were carried out at 40, 50 and 60 $^{\circ}$ C, for 20, 30, 40 and 50 min, based on previously published methods^{13,14}. The results showed that there were no significant differences between samples extracted at different temperatures and times by the PDMS/DVB fiber. A sample temperature of 50 $^{\circ}$ C and SPME extraction time of 0.5 h were finally selected.

Two types of coating fibers were investigated on the cultivar of 'Tengnian' (Fig. 1): 85 μ m (polyacrylate) and 65 μ m PDMS/DVB. It showed that the PDMS/DVB fibre had a good selectivity for substances with low to middle molecular weight and could detect more substances. Polyacrylate coating showed a better selectivity for substances with high molecular weight, but the baseline is elevating in the latter time. The two fibers showed a significant difference in the numbers of volatiles in Tengnian grapes (Fig. 2). Then the PDMS/DVB fibre was chosen in the following analytical procedure.

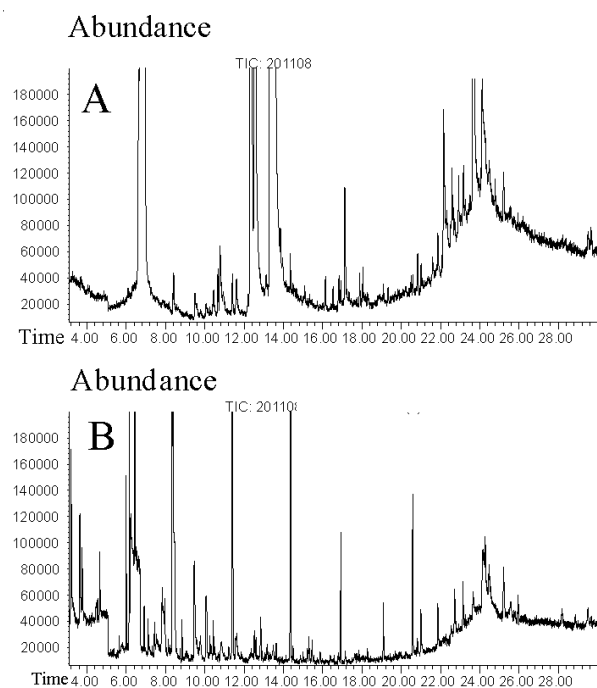


Fig. 1. Total ion chromatogram (TIC) of 'Tengnian' grape by GC-MS with the coating fiber: A. 85 μ m (PA) and B. 65 μ m PDMS/DVB

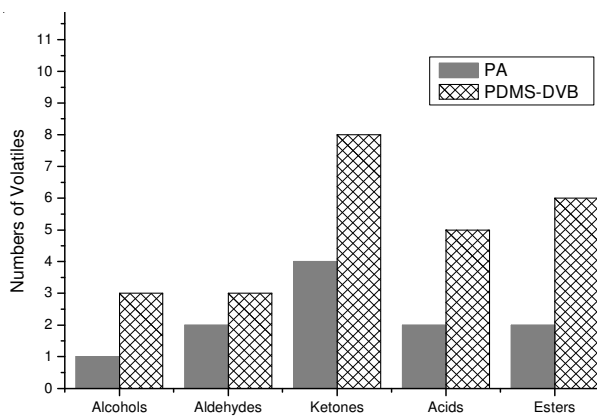


Fig. 2. Numbers of volatiles in Tengnian grape extracted by PDMS/DVB and PA

Types of volatiles compounds in four cultivars of table grape at different stage of storage: The samples of four cultivars table grape were extracted using SPME with subsequent analysis by GC-MS both at the beginning of storage and at the end of storage. In the initial stage, a total of 44 volatile compounds, including alcohols, carbonyls, esters and acids were found in the four cultivars (Table-1). Both the types and numbers of volatile compounds showed great difference among different grape varieties. There were 37 compounds identified in 'Tengnian', 30 in 'Longan', 30 in 'Cow's Teat' and 29 in 'Emerald non-nuclear'. Different types and contents of volatile compounds result in unique grape berry flavors.

There were much more alcohols identified in 'Cow's Teat' than in the other three cultivars. (E)-2-Hexen-1-ol had the highest content in 'Cow's Teat' and the relative content of (E)-2-hexen-1-ol reached 12.86 %. Trace were the alcohols detected in 'Longan'.

Aldehydes were the most abundant volatiles in the cultivar 'Cow's Teat' and 'Emerald non-nuclear'. The content of (E)-2-hexenal in the cultivar 'Cow's Teat' and 'Emerald non-nuclear' reached 48.25 and 28.45 %, respectively. There was no other aldehyde detected in 'Emerald non-nuclear' except for (E)-2-hexenal. 2-Hexenal (leaf aldehyde) as a main volatile compound in grape berry not only provides rich fragrance of fresh fruit and clean leaf, but also could inhibit the growth of mold¹⁵. Both the colours on grape berries of 'Cow's Teat' and 'Emerald non-nuclear' were green. This showed that the green cultivars of grape could have a higher content of (E)-2-hexenal than the cultivar of other colours.

There were many kinds of ketones in the four cultivars, but their total relative contents were all low. Acid levels, other than 6-octadecenoic acid, were relatively low in all grape cultivars. However, 6-octadecenoic acid only existed in the red cultivars. Only one kind of acid was detected in 'Emerald non-nuclear' and the relative acid content was no more than 1 %.

Esters were the most abundant volatiles in the 'Tengnian' and 'Longan' grape and the relative contents of ester reached 29.05 and 38.33 %. Ethyl caproate was the dominant ester in 'Tengnian', 'Longan' and 'Emerald non-nuclear', but it wasn't detected in 'Cow's Teat'. Ethyl caproate provided fruit sweet smell and was detected in many kinds and types of fruits, such as pineapple, pear, papaya, mango and strawberry¹⁶⁻¹⁸. 'Cow's Teat' was short of esters and acid, but the content of cyclohexene was relatively higher.

After 20 days of 20 °C storage, volatile compounds changed a lot in all the four cultivars (Table-2). The types of volatile compounds reduced from 37 to 14 in 'Tengnian', from 30 to 14 in 'Longan', from 30 to 16 in 'Cow's Teat' and from 29 to 16 in 'Emerald non-nuclear'.

In the initial stage of storage, (E)-2-hexen-1-ol was the general composition in the four cultivars except 'Longan', but disappeared in the final stage in 'Tengnian' and 'Emerald non-nuclear', while it's relative content in 'Cow's Teat' increased from 12.86 to 16.46 %. Phenylethyl alcohol was the general composition that appeared only in the final stage of storage. The content of (E)-2-hexenal was reduced in the two green cultivars accompanied with the fresh scent weaken during storage and disappeared in 'emerald non-nuclear' finally. Nonanal was the composition that emerged in the later storage stage

and provided the odor of sweet orange oil^{19,20} in the two green cultivars 'Cow's Teat' and 'Emerald non-nuclear'. Contents of 11-dodecen-2-one in 'Longan' and 'Cow's Teat' increased during storage. 4-Butylbenzoic acid emerged in 'Longan' at the final stage of storage.

The relative content of esters in the cultivar 'Emerald non-nuclear' increased more, for the contribution of two compounds ethyl *trans*-crotonate and ethyl caproate, which increased from 0 to 34.62 and 15.12 to 33.65 % and the total relative content of esters had reached 75.53 %. Several new esters also appeared in 'Longan' and 'emerald non-nuclear'. The 'Cow's Teat' still lacked of esters at the end of storage. In addition, the composition changed more in 'Longan', which showed from 7.86 % in the initial stage to 22.92 % in the final stage of storage.

Principal component analysis analysis: A principal component analysis (PCA) was performed to determine which the most important volatile were and non-volatile compounds on table grape before and after postharvest storage. This was used to establish relationships between storage stages and volatile compounds. The PCA can compress the data based on their similarities and differences, by reducing the number of dimensions without much loss of information and define the number of "principal components"²¹. In present case, the two first principal components (PCs) are sufficient to explain the maximum variation in all original dates. The corresponding loadings plot established the relative importance of each volatile component in the initial stage (Fig. 3A) and in the final stage (Fig. 3B) of storage. This analysis included alcohols, aldehydes, ketones, acids and esters.

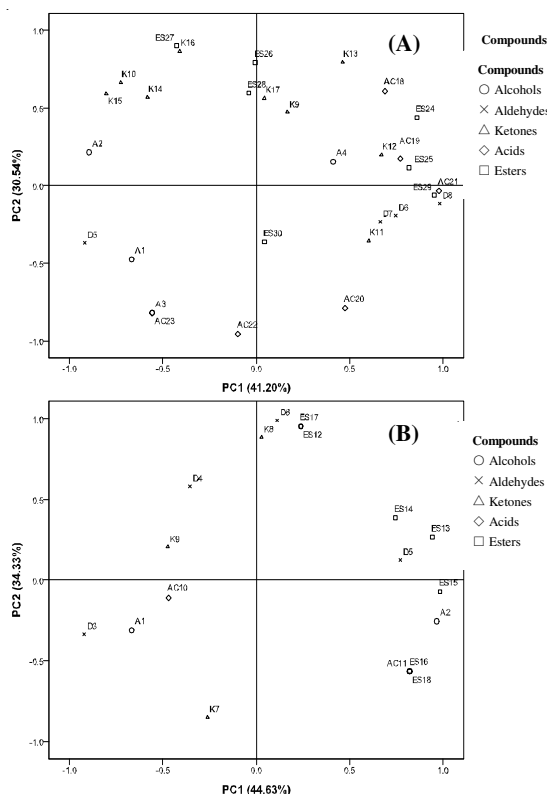


Fig. 3. Principal component analysis analysis of volatile compounds in 'Tengnian', 'Longan', 'Cow's Teat' and 'Emerald non-nuclear' during storage. (A) Loadings plot in the initial stage and (B) loadings plot in the later stage. Note: The numbers in figure (A) and (B) correspond to the volatile compound in Tables 1 and 2

TABLE-1
VOLATILE COMPOUNDS DETECTED IN FOUR CULTIVARS OF GRAPE IN INITIAL STORAGE

Code	Compound ^b	RT	Relative content in initial stage of storage (%) ^a			
			Tengnian	Longan	Cow's Teat	Emerald non-nuclear
Alcohols						
1	(E)-2-Hexen-1-ol	3.98	6.83 ± 1.35	ND ^c	12.86 ± 1.14	5.16 ± 0.85
2	4-Ethylamino-1-butanol	22.09	0.10 ± 0.02	0.41 ± 0.07	1.06 ± 0.42	1.58 ± 0.24
3	2-Dodecanol	23.64	ND	ND	0.84 ± 0.09	ND
4	1-Cyclohexyl-2-propen-1-ol	27.90	1.10 ± 0.04	ND	0.11 ± 0.08	ND
Aldehydes						
5	(E)-2-Hexenal	3.19	8.96 ± 0.96	ND	48.25 ± 2.45	28.45 ± 1.98
6	4-Methoxy-benzaldehyd	10.85	3.20 ± 0.56	1.72 ± 0.56	1.173 ± 1.44	ND
7	Dimethylaminoacetaldehyde dimethyl acetal	12.01	ND	0.30 ± 0.05	0.02 ± 0.08	ND
8	2-Methylundecanal	16.79	0.47 ± 0.04	0.49 ± 0.67	0.10 ± 0.04	ND
Ketones						
9	11-Dodecen-2-one	19.69	1.28 ± 0.25	0.04 ± 0.02	0.21 ± 0.08	0.53 ± 0.03
10	2-Pentadecanone	22.27	0.40 ± 0.07	0.10 ± 0.08	0.36 ± 0.06	0.77 ± 0.12
11	2-Nonadecanone	22.67	ND	1.77 ± 0.23	0.36 ± 0.07	ND
12	2-Hydroxy-1-cyclopentadecanone	23.41	2.91 ± 0.45	0.76 ± 0.11	ND	ND
13	Oxacyclotetradecan-2-one	24.86	0.10 ± 0.05	0.48 ± 0.09	ND	0.68 ± 0.12
14	2,15-Hexadecanedione	25.68	0.07 ± 0.02	0.50 ± 0.51	0.40 ± 0.07	1.31 ± 0.54
15	Cyclohexadecanone	26.37	0.17 ± 0.07	ND	0.31 ± 0.06	0.86 ± 0.11
16	6-Methyl-2-heptanone	26.70	1.19 ± 0.13	0.16 ± 0.07	0.38 ± 0.04	1.82 ± 0.21
17	6,10-Dimethylundecan-2-one	28.57	0.72 ± 0.05	ND	0.13 ± 0.04	0.39 ± 0.07
Acids						
18	3-Methoxypropionic acid	13.17	0.20 ± 0.05	0.30 ± 0.02	ND	0.21 ± 0.01
19	Egtazic acid	21.43	0.15 ± 0.03	0.06 ± 0.01	ND	ND
20	(E)-Traumatic acid	23.42	1.00 ± 0.23	0.87 ± 0.09	1.05 ± 0.06	ND
21	6-Octadecenoic acid	23.55	4.43 ± 0.58	7.51 ± 0.65	ND	ND
22	9-Hexadecenoic acid	25.14	1.10 ± 0.26	1.01 ± 0.34	2.50 ± 0.41	ND
23	Undecylenic acid	25.75	ND	ND	0.75 ± 0.09	ND
Esters						
24	Ethyl caproate	6.42	22.23 ± 1.32	30.61 ± 2.56	ND	15.12 ± 1.69
25	(E)-2-Hexenoic acid,ethyl ester	7.10	1.24 ± 0.32	3.60 ± 0.58	ND	0.90 ± 0.02
26	Phenylacetic acid ethyl ester	10.43	2.37 ± 0.14	ND	ND	1.87 ± 0.25
27	Crystal violet lactone	12.85	1.28 ± 0.32	ND	ND	3.21 ± 0.57
28	2-(4-Methylphenoxy)benzoic acid methyl ester	21.87	ND	1.96 ± 0.11	ND	2.48 ± 0.31
29	12-Octadecenoic acid methyl ester	23.57	1.06 ± 0.35	2.16 ± 0.24	ND	ND
30	Nervonic acid methyl ester	27.11	0.87 ± 0.12	ND	0.64 ± 0.08	ND
Others						
31	Cyclohexene	3.60	6.13 ± 0.71	ND	14.07 ± 1.06	8.42 ± 0.52
32	Limonene	6.96	ND	ND	0.60 ± 0.09	1.38 ± 0.21
33	Amodiaquine	7.69	0.44 ± 0.07	0.92 ± 0.25	0.20 ± 0.07	1.28 ± 0.08
34	2-Methoxyphenamine hcl	8.99	0.09 ± 0.02	0.42 ± 0.08	0.16 ± 0.02	0.44 ± 0.06
35	Naphthalene	9.46	8.89 ± 0.62	7.86 ± 0.84	2.20 ± 0.37	7.14 ± 0.69
36	Allyl phenyl ether	11.61	2.37 ± 0.35	2.73 ± 0.57	ND	ND
37	Ephedrine	14.56	0.63 ± 0.14	0.15 ± 0.06	0.47 ± 0.09	0.39 ± 0.06
38	N,N-Dimethylethylamine	19.73	0.54 ± 0.12	0.10 ± 0.05	0.04 ± 0.00	ND
39	2-Dimethylaminoethyl cyanide	21.19	ND	0.18 ± 0.39	0.12 ± 0.05	0.27 ± 0.04
40	Trans-1,4-Cyclohexanediamine	21.46	0.35 ± 0.07	ND	0.06 ± 0.01	0.73 ± 0.09
41	2,5-Dimethylpiperazine	23.39	0.92 ± 0.21	ND	0.41 ± 0.07	0.90 ± 0.14
42	Bisphenol A	24.21	9.09 ± 0.89	21.16 ± 1.35	10.18 ± 0.98	10.01 ± 1.22
43	2,4'-Bisphenol A	24.28	2.97 ± 0.42	8.41 ± 0.97	ND	2.58 ± 0.41
44	Pyrimidine	27.38	3.22 ± 0.22	3.24 ± 0.18	ND	1.12 ± 0.35

^aThe relative content of each compound was detected by the normalization method of peak area. ^bAnalytes were separated on an DB-5 capillary column (0.25 mm × 30 m × 1.0 μm) and identified by comparison with reference spectra (Wiley 5 and NIST 98 databases). ^c'ND' Indicates the volatile compound was not detected.

The first two principal components (PCs) explain 71.74 % of the total variance in the data of initial stage and 78.96 % of total variance in final stage. In the initial stage, some ketones (K) (2-nonadecanone, 2-hydroxy-1-cyclopentadecanone) were represented in the positive region of the first principal component factor, while other ketones were almost in the negative region of the second principal component factor. So ketones

were the main influence factors at the initial stage of storage. At the final stage, ketones also play an important role, for 11-dodecen-2-one and 2-nonadecanone were, respectively located in the negative and positive region of PC2 and 6,10-dimethylundecan-2-one was in the negative region of PC1. Most of the alcohols (A), such as (E)-2-hexen-1-ol, 4-ethylamino-1-butanol and 2-dodecanol were in the negative region of PC1

TABLE-2
VOLATILE COMPOUNDS DETECTED IN FOUR CULTIVARS OF GRAPE IN LATTER STORAGE

Code	Compound ^b	RT	Relative content in final stage of storage (%) ^a			
			Tengnian	Longans	Cow's Teat	Emerald non-nuclear
Alcohols						
1	(E)-2-Hexen-1-ol	3.65	ND ^c	ND	16.46 ± 0.98 ^c	ND
2	Phenylethyl alcohol	8.14	4.08 ± 0.35	15.26 ± 1.23	2.23 ± 0.31	7.02 ± 0.88
Aldehydes						
3	(E)-2-Hexenal	3.20	13.58 ± 1.21	ND	13.85 ± 0.82	ND
4	Nonanal	8.00	ND	ND	3.37 ± 0.47	3.52 ± 0.13
5	4-Methoxy-benzaldehyde	10.85	ND	2.63 ± 0.58	1.33 ± 0.29	2.30 ± 0.46
6	2-Methylundecanal	18.07	0.29 ± 0.09	ND	0.15 ± 0.03	1.59 ± 0.04
Ketones						
7	11-Dodecen-2-one	23.80	1.54 ± 0.04	2.08 ± 0.02	2.53 ± 0.01	1.00 ± 0.09
8	2-Nonadecanone	26.32	0.93 ± 0.17	0.27 ± 0.04	0.19 ± 0.05	1.26 ± 0.56
9	6,10-Dimethylundecan-2-one	27.32	0.26 ± 0.03	0.37 ± 0.07	1.26 ± 0.09	0.85 ± 0.11
Acids						
10	3-Methoxypropionic acid	5.27	2.78 ± 0.45	ND	0.27 ± 0.04	ND
11	4-Butylbenzoic acid	10.85	ND	4.89 ± 0.61	ND	ND
Esters						
12	Ethyl <i>trans</i> -crotonate	3.27	ND	ND	ND	34.62 ± 2.98
13	Ethyl tiglate	5.47	ND	2.20 ± 0.49	ND	1.98 ± 0.27
14	Ethyl caproate	6.46	27.36 ± 2.69	31.71 ± 1.87	ND	33.65 ± 4.12
15	Ethyl phenylacetate	10.43	ND	6.85 ± 0.98	ND	3.57 ± 0.16
16	Ethyl caprate	13.19	ND	3.84 ± 0.21	ND	ND
17	Ethyl laurate	16.47	ND	ND	ND	1.71 ± 0.25
18	Palmitic acid ethyl ester	21.92	ND	3.95 ± 0.29	ND	ND
Others						
19	1-Cyclopropylpropane	3.76	28.63 ± 3.78	ND	44.76 ± 2.97	ND
20	Limonene	6.95	3.02 ± 0.26	ND	1.56 ± 0.09	3.32 ± 0.52
21	Amodiaquine	7.73	7.09 ± 0.69	ND	0.92 ± 0.17	1.27 ± 0.26
23	Naphthalene	9.47	3.93 ± 0.57	22.92 ± 1.86	9.99 ± 1.07	ND
24	Dimethylaminopropionitrile	23.63	3.91 ± 0.45	2.48 ± 0.36	0.78 ± 0.09	0.42 ± 0.09
25	N-Isopropylmethylamine	25.53	2.60 ± 0.31	0.54 ± 0.06	0.35 ± 0.02	1.93 ± 0.31

^aThe relative content of each compound was detected by the normalization method of peak area. ^bAnalytes were separated on an DB-5 capillary column (0.25 mm × 30 m × 1.0 μm) and identified by comparison with reference spectra (Wiley 5 and NIST 98 databases). ^c'ND' Indicates the volatile compound was not detected.

at the initial stage and at final stage, the only two alcohols, (E)-2-hexen-1-ol and phenylethyl alcohol were located in the negative and positive region of PC1. This indicated that alcohols were also important both at initial stage and at final stage. All the esters (ES) were located either in the positive region (ethyl tiglate, ethyl caproate, ethyl phenylacetate, ethyl caprate, ethyl laurate and palmitic acid ethyl ester) of PC1 or in the positive region (ethyl *trans*-crotonate and ethyl laurate) of PC2 at final stage of storage, therefore, it was important in this phase.

Effect of related indexes on volatile compounds: Total sugar, total acid and sugar acid ratio could reflect some gustatory sense. These indexes also changed a lot during storage and the changing related to the altering of volatile compounds. Figs. 4-6 show the results for the changes of total sugar (°Brix), total acidity (titratable acidity, TA) and sugar acid ratio in different cultivars of grape berries during storage. Both the contents of total sugar and total acid in the cultivar 'Cow's Teat' were much higher than in the other three cultivars. This could be related to the lack of esters and acid in this cultivar (Table-1). The changing of total sugar and total acid increased steadily and sugar acid ratio showed a tendency of rising slightly in the first and then falling in the final stage in 'Cow's Teat'.

For the cultivar 'Tengnian', the changing of total sugar and total acid was different from the other three cultivars, which

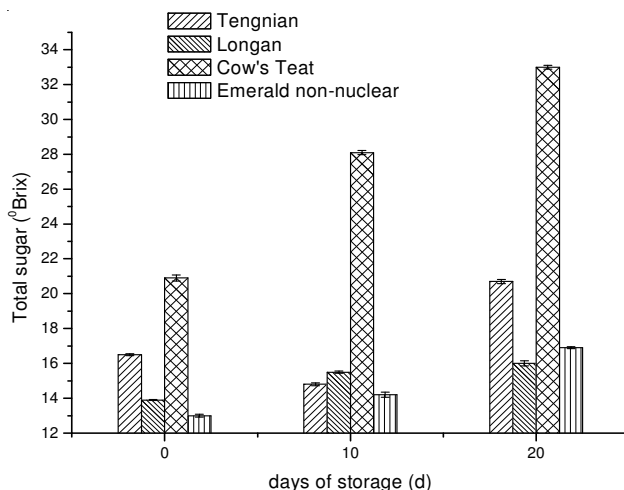


Fig. 4. Changes of total sugar in four cultivars of grape during storage at 20 °C and environmental humidity conditions. Vertical bars represent the standard errors of the means of triplicate samples

showed a tendency of falling first and then rising. The sugar acid ratio in this cultivar also showed the greatest change, which first increased then decrease. Comparison of Table-1 with Table-2 shows that the types of volatile compounds changed a lot in the cultivar 'Tengnian' between the initial stage and final stage of storage. In the later stage of storage, contents of

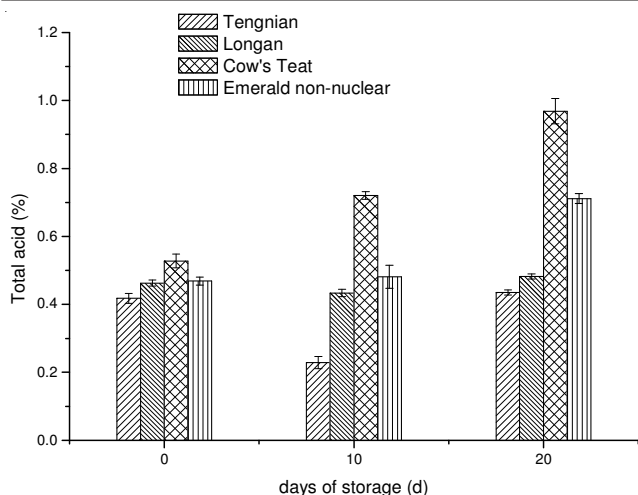


Fig. 5. Changes of total acid in four cultivars of grape during storage at 20 °C and environmental humidity conditions. Vertical bars represent the standard errors of the means of triplicate samples

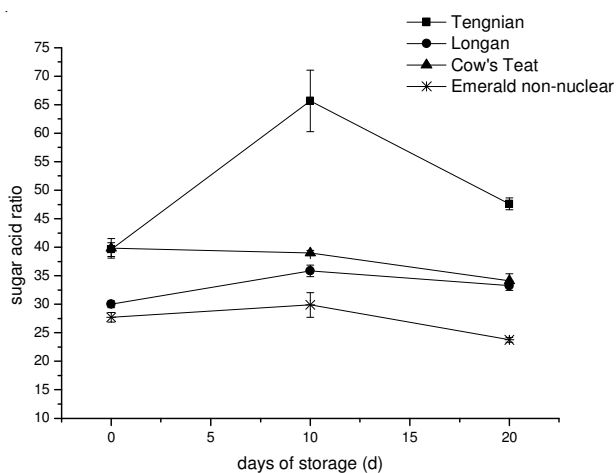


Fig. 6. Changes of sugar acid ratio in four cultivars of grape during storage at 20 °C and environmental humidity conditions. Vertical bars represent the standard errors of the means of triplicate samples

other compounds beside alcohols, aldehyde, ketones, acids and esters had increased from 32.67 to 49.18 %.

There were little changes in the contents of both total sugar and total acid in 'Longan' during storage and at the final stage the content of alcohols was much higher than in the initial stage. The contents of total sugar and total acid in 'Cow's Teat' increased steadily and the sugar acid ratio fell slightly at the final stage of storage. In this cultivar, the contents of aldehydes and acids in the final stage compared with the initial stage of storage decreased sharply from 49.54 to 18.70 % and from 4.3 to 0.27 %, respectively (Tables 1 and 2).

Conclusion

Composition of volatile compounds in the four cultivars of table grape, 'Tengnian', 'Longan', 'Cow's Teat' and 'Emerald non-nuclear' all changed a lot during postharvest storage and the changing depended on the cultivar used. Overall, the numbers of volatile compounds in all cultivars decreased during storage. (E)-2-Hexen-1-ol was the general alcohol composition in most cultivars of grape in the initial stage of

storage, but almost disappeared except in 'Cow's Teat' in the final stage. When fresh the green cultivars of grape had a higher content of (E)-2-hexenal than the red cultivars and the content difference between colours at the end of storage was little. The numbers of ketones in the four cultivars all reduced a lot during storage. The relative content of esters in the cultivar 'Emerald non-nuclear' increased more after storage, for the contribution of two compounds ethyl trans-crotonate and ethyl caproate. Both the contents of total sugar and total acid in the cultivar 'Cow's Teat' were much higher than in the other three cultivars no matter before or after storage. For the cultivar of 'Tengnian', the changing trend of total sugar and total acid was different with the other three cultivars.

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REFERENCES

1. Y. Deng, Y. Wu, Y. Li, P. Zhang, M. Yang, C. Shi, C. Zheng and S. Yu, *J. Food Eng.*, **78**, 500 (2007).
2. R.C. Soliva-Fortuny, N. Grigelmo-Miguel, I. Odriozola-Serrano, S. Gorinstein and O. Martín-Belloso, *J. Agric. Food Chem.*, **49**, 3685 (2001).
3. M. Blanch, M.T. Sanchez-Ballesta, M.I. Escribano and C. Merodio, *Food Chem.*, **129**, 724 (2011).
4. X. Meng, B. Li, J. Liu and S. Tian, *Food Chem.*, **106**, 501 (2008).
5. D. Rico, A.B. Martín-Diana, J.M. Barat and C. Barry-Ryan, *Trends Food Sci. Technol.*, **18**, 373 (2007).
6. E. Sánchez-Palomo, M.C. Díaz-Maroto and M.S. Pérez-Coello, *Talanta*, **66**, 1152 (2005).
7. E. Sánchez-Palomo, M.E. Alanón, M.C. Díaz-Maroto, M.A. González-Vinas and M.S. Pérez-Coello, *Talanta*, **79**, 871 (2009).
8. A. Bozdogan and A. Canbas, *Asian J. Chem.*, **21**, 2835 (2009).
9. C. Yang, Y. Wang, Z. Liang, P. Fan, B. Wu, L. Yang, Y. Wang and S. Li, *Food Chem.*, **114**, 1106 (2009).
10. P. Hernández-Orte, M. Cersosimo, N. Loscos, J. Cacho, E. García-Moruno and V. Ferreira, *Food Chem.*, **107**, 1064 (2008).
11. C.L. Arthur and J. Pawliszyn, *Anal. Chem.*, **62**, 2145 (1990).
12. H. Prosen and L. Zupancic-Kralj, *TrAC Trends Anal. Chem.*, **18**, 272 (1999).
13. W. Kang, Y. Xu, L. Qin and Y. Wang, *J. Inst. Brew.*, **116**, 70 (2010).
14. X.- Li, L. Kang, J.- Hu, X.- Li and X. Shen, *Agric. Sci. China*, **7**, 1451 (2008).
15. D.D. Archbold, T.R. Hamilton-Kemp, A.M. Clements and R.W. Collins, *HortScience*, **34**, 705 (1999).
16. C. Balbontin, C. Gaete-Eastman, M. Vergara, R. Herrera and M.A. Moya-Leon, *Postharvest Biol. Technol.*, **43**, 67 (2007).
17. J.A. Pino, J. Mesa, Y. Muñoz, M.P. Martí and R. Marbot, *J. Agric. Food Chem.*, **53**, 2213 (2005).
18. P. Wu, M.-C. Kuo, T.G. Hartman, R.T. Rosen and C.-T. Ho, *J. Agric. Food Chem.*, **39**, 170 (1991).
19. Y. Qiao, B.J. Xie, Y. Zhang, Y. Zhang, G. Fan, X.L. Yao and S.Y. Pan, *Molecules*, **13**, 1333 (2008).
20. C.B. Faturi, J.R. Leite, P.B. Alves, A.C. Canton and F. Teixeira-Silva, *Prog. Neuro-Psychoph.*, **34**, 605 (2010).
21. J. Rodriguez-Campos, H.B. Escalona-Buendía, I. Orozco-Avila, E. Lugo-Cervantes and M.E. Jaramillo-Flores, *Food Res. Int.*, **44**, 250 (2011).