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Volatile Compounds of Orange Wines Produced with and without Peel Contact

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Abstract The present study focused on the effects of peel contact on the volatile compounds of orange wines. The volatile compounds were analyzed by sensory and instrumental analyses. Solid-phase microextraction (SPME) was used for extraction of volatile compounds. A total of 19 and 27 volatile compounds were identified in without and with peel contact wines respectively. Esters were quantitatively the dominant group of volatile compounds in without peel contact wines, while terpenes were the most abundant compounds in peel contact wines. Totally 11 and 14 new formed compounds were found in without and with peel contact wines, mainly were esters, alcohols, and acids. According to sensory analysis, the peel contact wine showed a more citrus-like and fruity aroma than the wines without peel contact.

Keywords: orange, wine, volatile compound, peel contact, solid-phase microextraction

Introduction

Citrus flavors are the most popular of all soft drinks flavors, and orange flavor is the favorite of consumers worldwide (1). Up to now, numerous studies have widely reported the volatile compounds in orange juice and essential oil. Esters, aldehydes, ketones, terpenes, and alcohols were the important contributors to orange juice flavor (2).

Aroma is one of the important factors determining wine character and quality. Previous studies showed that over 1,300 volatile compounds were identified in alcoholic beverages (3). These volatile compounds mainly were higher alcohols, aldehydes, ketones, esters, acids, monoterpenes, and C_{13}-norisoprenoids (4). The flavor of grape wine has been widely investigated and depends on the grape variety used, the aroma produced during fermentation and those developed during the ageing process (5), as well as the choice of production method. The must skin contact technique before fermentation has been proposed to increase the aroma of white wines (6). Contact between juice and peel, prior to fermentation, generally results in higher concentrations of potential aroma compounds both in juice and wine (7). Selli *et al*. (8) studied that peel-contact treatment could be used to enrich Narince wine both in free and bound aroma compounds. Palomo *et al*. (4) concluded that pre-fermentation maceration of musts with grape peel, together with glycosidic-enzyme treatment of wines, provides a viable alternative to traditional methods for enhancing the varietal character of Albillo wines. Similar result was also obtained by them in muscat wines (9).

It is reported that oranges, mandarin, and grapefruit have been used for winemaking. Researches on orange wines have seldom been reported (10,11). Selli *et al*. (3) studied the flavor components of orange wine made from a Turkish cv. Kozan using spontaneous yeasts. Subsequently, they investigated the most odor-active volatile compounds of the wines and found that ethyl butanoate, 3-methyl-1-pentanol, linalool, γ-butyrolactone, 3-(methylthio) propanol, geraniol, and 2-phenylethanol were the most important contributors to the aroma of the wines (12). Wine aroma varied from climate, region, fruit variety, yeast, as well as wine-making techniques. However, there was no studies focused on the effect of peel contact on the volatile compounds of orange wines.

Solid-phase microextraction (SPME) was developed by Pawliszyn and coworkers, and this technique has been applied to a wide range of environmental and food applications (13,14). It has been extensively used for the analysis of orange juice aroma with the characteristics of being rapid, solventless, and relatively inexpensive (15).

'Qixue cheng' is an orange cultivar belonging to the subgroup *Citrus sinensis* Osbeck, and is widely cultivated in Yichang, Hubei. This fruit harvested in January and February has very good commercial quality for processing with a good balance of sweet taste, a refreshing aroma, and very novel color. No studies worked on the orange wines made from this cultivar.

The aim of the following study was to investigate the effects of peel contact on volatile compounds of orange wine. In addition, sensory evaluation of the orange wines was performed by using descriptive flavor profile analysis.

Materials and Methods

Reagents and reference samples Standards of *n*-paraffins (C_6-C_{20}) were purchased from Sigma-Aldrich (St Louis, MO, USA). The aroma standards hexanal, benzaldehyde, *d*-limonene, nonanal, ethyl acetate, α-terpinene, isoamyl acetate, ethyl propanoate, copaene, sabinene, β-elemene, β-citral, carvone, (E)-3-hexen-1-ol, geranyl acetate, linalool, α-terpineol, and valencene were gifts from Gld-boton

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Essential Company (Shenzhen, Guangdong, China). Ethyl butanoate, β-myrcene, 2-hexenal, α-pinene, methyl octanoate, ethyl octanoate, 1-octen-3-ol, 1-hexanol, ethyl 3-hydroxyhexanoate, benzyl alcohol, hexanoic acid, δ-cadinene, ethyl laurate, decanal, undecanal, nootkatone, γ-terpinene, 4-terpineol, *cis*-carveol, ethyl 2-methylbutanoate, α-cubebene, ethyl hexanoate, caryophyllene, 2-phenylacetaldehyde, 1-octanol, phenylethyl alcohol, 1-pentanol, octanoic acid, ethyl decanoate, and phenethyl acetate were obtained from Fluka (Buchs, Switzerland). The water used in the study was purified by a Millipore-Q system (Millipore Corp., Saint-Quentin, France). An internal standard solution (IS) of cyclohexanone, 99.5% purity (Fluka) in ethyl alcohol was prepared at a concentration of 0.946 mg/mL.

Wine preparation Laboratory fermentations using 3-L vessels were used for wine producing. The mature oranges of 'Qixue cheng' variety were purchased from Yichang city which were harvested in the middle of January (China). Fruits were washed and dried, and then were divided into 2 batches.

One batch was treated in the way without peel contact. The pulp was obtained by hand separation from the peels, and was extracted into juice using a centrifugal juice extractor. The finished juice had a Brix value of 10°Bx, a pH value of 4.24, a total acid content of 0.51%, a Brix/acid ratio of 19.61 and juice content of 41.56%. Another batch was used for the peel contact experiments. The intact oranges were also extracted into juice using a centrifugal juice extractor. The 2 orange juices were then diluted with water at a ratio of 1.5:1 (juice:water) and 50 mg/L potassium metabisulfite was added to the juice. Before the alcoholic fermentation, 192 g/L sugar was added to reach 22°Bx.

Fermentation was performed by inoculating active dry yeast (Angel, Yichang, China) at 20°C. The yeast was activated in 2% sugar solution at 35°C for 1 hr. The activated yeast (2 g/kg) was then added to the 2 orange juices.

A model orange juice was also prepared for fermentation as control wine containing the matrix compounds (16.8 g/L fructose, 16.1 g/L glucose, 0.482 g/L vitamin C, 3.8 g/L citric acid, 50 mg/L potassium metabisulfite, and 198 g/L sugar). The pH of the model juice was adjusted to 4.24 using 0.1 N NaOH. Inoculated fermentation was applied for the control wine making as described above. Each fermentation was performed in duplicate.

Compositions and color analysis of control and orange wines The pH value was measured using a digital pH meter (Orion A410+; Thermo Electron Corporation, Woburn, MA, USA). Total acidity was determined by titration of 10 mL orange juice or wines with a solution of 0.1 N NaOH. Total sugar was measured using anthrone-sulfuric acid method. Reducing sugar was measured according to the method of Haixia *et al*. (16). Ethyl alcohol and total SO_2 was determined in orange wines (17). Orange juice and wines color (L*, a*, and b* values) were recorded using a Hunter Lab color-Flex 45/0 Spectrophotometer (Hunter Associates Laboratory, Inc., Reston, VA, USA). Each determination was performed in duplicate. Results are expressed as mean±standard deviation (SD).

Extraction of the volatile compounds The SPME manual device equipped with a 50/30 μm DVB/CAR/PDMS fiber (Supelco, Bellfonte, PA, USA) was used for extraction of orange juice and orange wines. The fiber was conditioned in gas chromatography (GC) injector port at 270°C for 1 hr prior to use. Ten mL of orange juice and orange wines with 3.6 g NaCl, previously added to 50 μL of cyclohexanone (0.946 mg/mL of ethyl alcohol) as an internal standard (IS) to each sample, was placed into a 20-mL vial containing a microstirring bar. The sample was equilibrated at 40°C for 15 min and extracted by DVB/CAR/PDMS fiber for 40 min at the same temperature under stirring (500 rpm). After extraction, the fiber was inserted into the injection port of GC to desorb the analytes for 5 min. Each analytical sample was measured in duplicate.

Sensory analysis of control and orange wines Descriptive flavor profile analysis was performed by 9 assessors (7 females and 2 males) from College of Food Science and Technology, Huazhong Agricultural University. Most of the assessors were previously trained in sensory evaluation techniques and had experience in gas chromatography-olfactometry (GC-O). Panelists were first familiarized with the 2 orange wines and control wine and asked to agree on a common list of 9 descriptors (fruity, citrus-like, orange, grassy, minty, floral, vanilla, alcohol, and spicy). All of the 9 assessors were then trained to smell the standards of the 9 consensual odor descriptors. They had to memorize the odor and then describe it using the descriptors list. Five mL of each sample was placed into a 10-mL coded flask for sensory tests. About 2 cm of the extremity of the fragrance blotter paper (142×6 mm) was immerged into the wine for 0.5 min and then presented to the assessors. The tests were performed at room temperature. The intensity of each character was evaluated on a 1-9 scale (1=very weak intensity, 3=weak intensity, 5=moderate intensity, 7=strong intensity, and 9=very strong intensity) (12). All tests were performed in duplicate.

GC-mass spectrometry (GC-MS) analysis of volatile compounds Volatile compounds were subjected to GC analysis on an Agilent 6890N GC coupled to an Agilent 5975B mass spectrometer (Agilent Technologies, Santa Clara, CA, USA), and equipped with a J&W HP-5MS fused silica capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness). Mass spectral ionization was set at 230°C. The mass spectrometer was operated in the electron ionization mode at a voltage of 70 eV. The flow rate of helium on HP-5MS column was 1.2 mL/min. A 0.75 mm liner was used and analysis performed in the splitless mode and injector temperature was 250°C. The column was held at 40°C for 3 min, and then increased from 40 to 160°C at 3°C/min, held at 160°C for 2 min, and finally increased to 220°C at a rate of 8°C/min, held for 3 min.

Identification of compounds detected by GC-MS analysis was done by comparing mass spectra and retention indices (RI) with the authentic standards and published data, as well as by comparing their mass spectra with the MS library of Wiley7.0 and NIST 0.5. Retention indices were calculated using a mixture of *n*-paraffin C_6-C_{20} as standards.

Semi-quantitative determinations were obtained by using cyclohexanone as an IS. The contents of the volatile compounds were calculated from the GC-peak areas relating to the GC-peak area of the IS.

Statistical analysis The statistical significance of the effect on the flavor of the wines produced with and without peel contact was determined by one-way analysis of variance (ANOVA). The mean rating and Fisher's least significant difference (LSD) for each sensory descriptor were calculated by ANOVA. Statistical analyses were done with the SPSS 13.0 for Windows statistical package (Chicago, IL, USA).

Results and Discussion

Sensory analysis of orange wines The sensory analysis of the orange wines were performed by 9 panelists, using 9 descriptors (fruity, citrus-like, orange, grassy, minty, floral, vanilla, alcohol, and spicy) previously agreed upon as the best for describing sensorial characteristics of wines, which were generated mainly by our panelists as well as the published papers (9,12).

The average aroma-intensity scores of the wines produced with and without peel contact on a 'spider-web' graph are shown in Fig. 1. As shown in the figure, the flavor profiles of the 3 wines are similar. It's in agreement with the result of statistical analysis that the one-way ANOVA analysis on the mean scores of each sensory descriptor showed no significant differences ($p>0.05$). Nevertheless, a distinct difference on the total aroma between the wines produced with and without peel contact was perceived by all panelists. The peel contact wine showed a more citrus-like and fruity aroma than the wines without peel contact. In other words, peel contact process enhanced the sensory attributes and gave rise to the aromas perceived more comfortable than the wines without peel contact. Similar findings have been reported in other studies (5,9).

Among these 9 descriptors, alcohol was the strongest flavor of the 3 wines with the highest scores. The other descriptors (orange, grassy, minty, floral, vanilla, and spicy) were perceived very weak with low scores in all the 3 wines. Similarly, the fruity and citrus-like aroma of the control wine and without peel contact wine were also perceived very weak, while these 2 descriptors were stronger in peel contact wine with relatively high scores.

Compositions and color analysis of orange wines The chemical properties, compositions, and colors of the control and orange wines are shown in Table 1. The differences of the compositions and color of the 2 orange wines were not significant. This indicates that there was minor effect of peel contact on the compositions and color of orange wine. There were some differences on the total acidity and sugar between the control wine and orange wines. The pH value of the control wine increased a lot after fermentation, while it was stable in the orange wines. And this mainly because the orange juice is a complex buffer system, the pH value of the juice may be more stable than the model juice.

Volatile compounds of pulp and peels of oranges Volatile compounds in pulp and peels in Qixue oranges analyzed by SPME-GC-MS are shown in Table 2. A total of 31 and 32 volatile compounds were respectively identified in pulp and peels with a total concentration of 21 mg/L and 1,221 mg/kg. Seventeen and 19 terpenes was found in pulp and peels, respectively, and they were the most abundant compounds representing 91 and 98% of their total volatile compounds contents in pulp and peels. Among these terpenes, *d*-limonene was the most abundant compound both in pulp and peels, accounting for 74 and 77% of total concentrations, respectively.

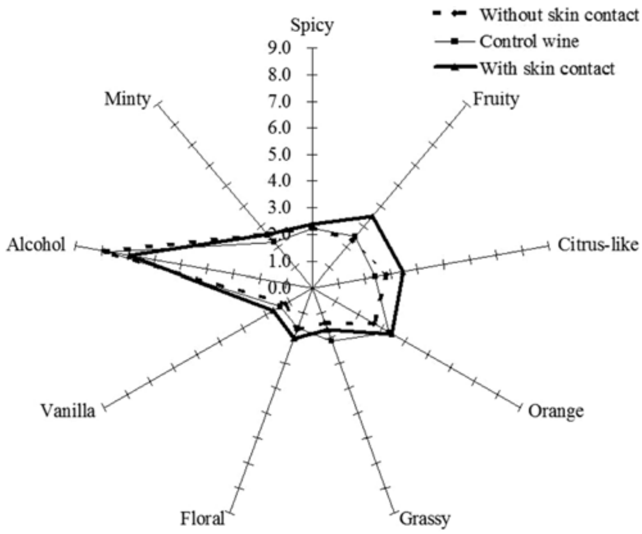

Fig. 1. Sensory descriptive analyses of orange wines. Mean scores of 9 judges (n=2).

Totally 8 esters, 4 aldehydes, 1 alcohol, and 1 ketone were identified in pulp, and 6 esters, 5 aldehydes, and 2 ketones were found in peels. There was a great difference on the volatile compounds between pulp and peels. Only 18 compounds were found both in pulp and peels, including 12 terpenes, 3 esters, 2 aldehydes, and 1 ketone.

Volatile compounds of orange wines Mean values of concentrations and standard deviations of the volatile compounds of control and orange wines are shown in Table 2. A total of 19 and 27 volatile compounds was identified in without and with peel contact orange wines with a total concentration of 81,447 and 353,293 μg/L, respectively.

Volatile compounds of orange wines without peel contact Being different from the volatile compounds of the pulp, esters were quantitatively the dominant group of volatile compounds in without peel contact wines, accounting for 46% of the total volatile compounds with a concentration of 37,195 μg/L. Totally 10 esters were found in this wine. Ethyl acetate, ethyl butanoate, ethyl 2-methylbutenoate, and ethyl octanoate were the 4 esters detected also in pulp. Ethyl acetate was considered as index of quality in the aromatic fraction of orange juice (2). While the concentrations of these esters in this orange wine were lower than pulp, and this indicates that these esters decreased after fermentation, except for ethyl octanoate.

Ethyl propanoate, ethyl 2-methylpropanoate, ethyl 2-butanoate, and ethyl 3-hydroxyhexanoate were only found

Table 1. Compositions and color analysis of control and orange wines

	Control wine	Orange wine	
		Without skin contact	With skin contact
Density (20ºC/20ºC)	0.9934±0.00	0.9823±0.00	0.9795±0.00
Total acidity[1)] (g/L)	5.8±0.10	4.0±0.20	4.1±0.11
pH	3.93±0.07	4.03±0.02	4.08±0.03
Alcohol (%, v/v)	8.2±0.12	10.5±0.15	10.2±0.13
Reducing sugar (g/L)	26.5±0.51	1.6±0.11	3.1±0.10
Total sugar (g/L)	67.1±0.22	1.6±0.10	7.8±0.21
Total SO_2 (mg/L)	29.4±0.24	0.9±0.09	2.4±0.14
Color			
L*	85.51±0.11	76.47±0.49	63.23±0.41
a*	-11.86±0.21	-7.30±0.17	-1.68±0.13
b*	27.84±0.24	32.42±0.31	34.71±0.26

[1)]Citric acid.

in pulp and absent in without peel contact wine due to their high volatility. While isoamyl acetate, ethyl hexanoate, ethyl benzoate, diethyl succinate, ethyl decanoate, and ethyl laurate were new formed esters in without peel contact wine. They are considered to be the primary metabolites of yeast sugar and amino acid metabolism during fermentation (18).

Most of the terpenes disappeared after winemaking. Only *d*-limonene, terpinene-4-ol, and valencene were identified in without peel contact wine with a total concentration of 8,421 μg/L. The content of *d*-limonene decreased after fermentation, while terpinene-4-ol and valencene increased in this course. Terpinene-4-ol was also found in the orange wines made from a Turkish cv. Kozan and was considered to be the aroma-active compound of this orange wine with a rancid aroma (12).

2-Ethylhexanol and 2-phenylethanol were the 2 alcohols found in without peel contact wine with a total concentration of 34,929 μg/L, accounting for 43% of the total content, and was the 2nd most abundant compounds. They were new formed compounds in without peel contact wine. These compounds are mainly produced by yeast during fermentation. 2-Phenylethanol was the most abundant compound, accounting for 43% of the total volatile compounds. Similar results were also obtained in some grape wines (19). It might be a very important contributor to the overall aroma of this wine due to its odor threshold values in hydro-alcoholic solution was 10,000 μg/L (20). This compound was also found and considered as an aroma-active alcohol in Kozan orange wines with a floral and rose odor (12).

2-Phenylacetaldehyde, hexanoic acid, and geranyl acetone were the other 3 new formed compounds in without peel contact wine. Benzaldehyde increased a lot and it might also be formed during fermentation.

Volatile compounds of orange wines with peel contact As shown in Table 2, a total of 27 volatile compounds were identified in with peel contact wine, including 10 terpenes, 9 esters, 6 alcohols, 1 ketone, and 1 acid.

Terpenes were the major volatile compounds with the highest concentration of 178,368 μg/L, representing 50% of the total volatile compounds. It is in agreement with the orange pulp and peels. These components are considered to be the most abundant compounds in the peel oil of the oranges and important contributors to the aroma in orange juice (21,22). Among these terpenes, *d*-limonene was the most abundant. It has a weak, citrus-like aroma, and is considered one of the major contributors to orange flavor if it is under 190 ppm (23,24). This indicates that *d*-limonene could contribute active to the total aroma of this wine. β-Myrcene, *d*-limonene, linalool, terpinene-4-ol, α-terpineol, *cis*-carveol, valencene, and δ-cadinene were the terpenes present both in pulp and wines with peel contact. While α-terpinolene and β-terpineol were new formed compounds in this wine.

Alcohols were the second most abundant compounds with a total concentration of 98,203 μg/L, accounting for 28% of the total concentrations. These higher alcohols are found as quantitatively the largest group of flavor compounds in alcoholic beverages, and are a secondary product of alcoholic fermentation (25). It is reported that concentrations of higher alcohols below 300 mg/L contribute a desirable level of complexity to wine, whereas concentrations exceed 400 mg/L can have a detrimental effect (26). They are formed during fermentation from keto acids produced either catabolically, involving degradation of an amino acid via the so-called Ehrlich pathway, or anabolically via the biosynthesis route from the carbon source (25). Totally 6 alcohols were identified in this wine: 1-pentanol, (E)-3-hexen-1-ol, 1-hexanol, 1-heptanol, 1-octanol, and 2-phenylethanol. None of them were found in orange pulp or peels. Among these alcohols, 1-pentanol, (E)-3-hexen-1-ol, 1-hexanol, 1-octanol, and 2-phenylethanol were also identified in Kozan orange wines, and (E)-3-hexen-1-ol, 1-octanol, and 2-phenylethanol were considered as aroma-active compounds with green-floral, floral, and citrusy-sweet aroma, respectively (12).

Totally 9 esters were identified in peel contact wines with a total concentration of 74,477 μg/L. Ethyl acetate, ethyl butanoate, ethyl 3-hydroxyhexanoate, and ethyl octanoate were also present in orange pulp or peels. Whereas ethyl hexanoate, ethyl heptanoate, ethyl benzoate, ethyl decanoate, and ethyl laurate were only found in peel contact wine and could be considered as new formed compounds by yeast during fermentation.

Table 2. Volatile compounds in orange and orange wine

Compound	RI[1)]	Content					ID[2)]
		Orange		Wine			
		Pulp (μg/L)	Peels (μg/kg)	Control wine (μg/L)	Without peel contact (μg/L)	With peel contact (μg/L)	
Terpenes							
α-Thujene	927	20.9±5.4[3)]	ND	ND	ND	ND	b
α-Pinene	932	94.1±11.2	13,587.0±521	ND	ND	ND	a
β-Phellandrene	974	43.7±10.5	2,425.0±292	ND	ND	ND	b
Sabinene	976	ND	1,933.0±245	ND	ND	ND	a
β-Myrcene	993	164.0±23.6	7,534.0±267	ND	ND	538.0±81	a
α-Terpinene	1,018	8.8±3.0	ND	ND	ND	ND	a
d-Limonene	1,035	15,124.0±239.4	942,829.0±1,143	ND	1,857.0±102	67,406.0±991	a
γ-Terpinene	1,061	17.3±4.0	2,114.0±395	ND	ND	ND	a
α-Terpinolene	1,092	ND	ND	ND	ND	97.0±15	b
Linalool	1,113	ND	1,820.0±296	ND	ND	7,295.0±630	a
trans-Limonene oxide	1,148	ND	7,201.0±1,025	ND	ND	ND	b
β-Terpineol	1,154	ND	ND	ND	ND	2,130.0±219	b
Menthol	1,178	13.4±5.5	ND	ND	ND	ND	b
Terpinene-4-ol	1,182	11.9±3.0	696.0±132	ND	182.0±21.8	46,547.0±714	a
α-Terpineol	1,196	5.8±1.8	ND	ND	ND	46,783.0±804	a
cis-Carveol	1,225	15.0±4.0	740.0±297	ND	ND	1,582.0±219	a
cis-Geraniol	1,261	ND	1,009.0±336	ND	ND	ND	b
α-Cubebene	1,354	13.9±0.4	1,709.0±416	ND	ND	ND	a
Copaene	1,380	ND	2,741.0±345	ND	ND	ND	a
β-Elemene	1,396	41.1±9.8	5,563.0±529	ND	ND	ND	a
Alloaromadendrene	1,455	ND	6,350.0±508	ND	ND	ND	b
Caryophyllene	1,459	57.9±12.7	8,462.0±774	ND	ND	ND	a
α-Selinene	1,492	29.3±8.5	ND	ND	ND	ND	b
Valencene	1,502	3,073.0±87.4	185,464.0±7,680	ND	6,382.0±588	5,908.0±517	a
δ-Cadinene	1,529	23.8±6.1	8,281.0±409	ND	ND	82.0±8.7	a
Caryophyllene oxide	1,572	ND	2,521.0±735	ND	ND	ND	a
Esters							
Ethyl acetate	628	135.0±17.4	266.0±27.3	ND	131.0±35.6	5,510.0±144	a
Ethyl propanoate	714	57.4±5.5	ND	ND	ND	ND	a
Ethyl 2-methylpropanoate	751	38.7±6.8	ND	ND	ND	ND	b
Ethyl butanoate	802	429.0±10.9	ND	ND	211.0±26.7	1,428.0±51	a
Ethyl 2-butanoate	844	38.2±0.7	ND	ND	ND	ND	b
Ethyl 2-methylbutanoate	849	395.0±71.3	ND	ND	ND	ND	a
Isoamyl acetate	884	ND	ND	1,443±102	4,326.0±233	ND	a
Ethyl 2-methylbutenoate	948	ND	ND	ND	88.0±12.4	ND	a
Ethyl hexanoate	1,007	ND	ND	8,542±147	4,788.0±125	23,967.0±821	a
Ethyl heptanoate	1,105	ND	ND	ND	ND	280.0±58	b
Methyl octanoate	1,134	ND	280.0±86	ND	ND	ND	a
Ethyl 3-hydroxyhexanoate	1,135	339.0±74	269.0±47	ND	ND	2,160.0±291	a
Ethyl benzoate	1,178	ND	ND	849.0±73.7	525.0±95	3,112.0±556	b
Diethyl succinate	1,191	ND	ND	457.0±74.2	312.0±39	ND	b
Hexyl butanoate	1,196	ND	977.0±186	ND	ND	ND	b
Ethyl octanoate	1,201	10.6±4.1	3,484.0±691	23,842.0±130	11,163.0±272	31,395.0±978	a
Geranyl acetate	1,369	ND	2,120.0±920	ND	ND	ND	a
Ethyl decanoate	1,403	ND	ND	5,026.0±115	14,157.0±158	5,764.0±427	a
Ethyl laurate	1,502	ND	ND	443.0±78	1,494.0±133	861.0±147	a
Alcohols							
1-Pentanol	759	ND	ND	ND	ND	78,054.0±891	a

Table 2. Continued

Compound	RI[1)]	Content					ID[2)]
		Orange		Wine			
		Pulp (μg/L)	Peels (μg/kg)	Control wine (μg/L)	Without peel contact (μg/L)	With peel contact (μg/L)	
(E)-3-Hexen-1-ol	865	ND	ND	ND	ND	270.0±100	a
1-Hexanol	875	ND	ND	ND	ND	2,611.0±377	a
1-Heptanol	981	ND	ND	ND	ND	870.0±31	b
1-Octen-3-ol	985	8.2±1.0[3)]	ND	ND	ND	ND	a
2-Ethylhexanol	1,039	ND	ND	ND	164.0±47.1	ND	b
1-Octanol	1,081	ND	ND	ND	ND	117.0±38	a
2-Phenylethanol	1,127	ND	ND	41,890.0±128	34,765.0±160	16,281.0±815	a
Aldehydes and ketones							
Hexanal	801	83.4±19.7	1,712.0±160	ND	ND	ND	a
2-Hexenal	853	204.0±58.2	2,914.0±224	ND	ND	ND	a
Benzaldehyde	962	2.2±0.8	ND	ND	220.0±21.4	ND	a
2-Phenylacetaldehyde	1,052	ND	ND	ND	108.0±12.2	ND	a
Nonanal	1,108	43.7±7.8	ND	ND	ND	ND	a
Decanal	1,212	ND	3,928.0±312	ND	ND	ND	a
β-Citral	1,248	ND	442.0±188	ND	ND	ND	a
Carvone	1,251	ND	1,034.0±468	ND	ND	783.0±136	a
Undecanal	1,311	ND	170.0±93	ND	ND	ND	a
Geranyl acetone	1,461	ND	ND	ND	199.0±42.3	ND	b
Nootkatone	1,819	16.9±3.2	298.0±86	ND	ND	ND	a
Acids							
Hexanoic acid	1,013	ND	ND	1,448.0±201	375.0±78.2	1,462.0±356	a
Octanoic acid	1,279	ND	ND	3,625.0±181	ND	ND	a

1)RI, linear retention index on HP-5MS column.
2)Identification: a, comparison of mass spectra and retention index with authentic standards; b, comparison of mass spectra and retention index with published data and MS library of Wiley7.0 and NIST 0.5.
3)Mean±SD; ND, not detected.

Hexanoic acid was the only acid identified in wines with peel contact, and was absent in orange pulp or peels. Volatile fatty acids are important contributors to the *fermentation bouquet* of wines, and were primary metabolites of yeast sugar and amino acid metabolism (19).

Comparisons of volatile compounds of orange wines produced with and without peel contact Volatile compounds in the orange wines showed an obvious difference. It was in agreement with the result of sensory analysis.

As described above, esters (46%) were the most abundant compounds in wines without peel contact, while terpenes (50%) were quantitatively the dominant group of volatile compounds in peel contact wines. This might be the reason for the difference on the total aroma of the 2 wines, due to terpenes have a low olfactory threshold and are generally associated with floral and citric aromas (20). Palomo *et al.* (4) found that maceration of must with peel doubled the amount of these compounds in Albillo wines. Similar finding was also obtained in the present study that peel contact enhanced the concentrations of terpenes of orange wines. These terpenes mainly came from orange peels due to most of them were also found in orange peels except for α-terpinolene and β-terpineol. The presence of linalool, β-terpineol, terpinene-4-ol, α-terpineol, and *cis*-carveol in peel contact wine indicated that they might be from the peels or released from the glycosidic volatile precursors. α-Terpineol is a well known off-flavor compound present in stored citrus products formed from *d*-limonene or linalool (27), and is also considered as an indicator of the age of orange juice and its presence becomes a problem at levels higher than 2 ppm (28).

d-Limonene, terpinene-4-ol, and valencene were the 3 terpenes identified both in orange wines produced without and with peel contact. No terpenes were found in control wine. This indicates that terpenes might not be formed during fermentation. However they might be formed or released from the potential glycosidic precursors during orange winemaking.

Most of the esters were found both in the 2 wines, such as ethyl acetate, ethyl butanoate, ethyl hexanoate, ethyl benzoate, ethyl octanoate, ethyl decanoate, and ethyl laurate. While isoamyl acetate, ethyl 2-methylbutenoate, and diethyl succinate were only found in without peel contact wine, and ethyl heptanoate and ethyl 3-hydroxyhexanoate were present only in peel contact wine. Nisperos-Carriedo and Shaw (2) reported that ethyl acetate and ethyl butyrate were considered as indices of quality in the aromatic fraction of orange juice. And ethyl acetate may contribute a pleasant, fruity fragrance to the general wine aroma at concentrations lower than 150 mg/L (25). Esters (46%) were the main volatile compounds in control wine. Totally 7 esters were identified with a total concentration of 40,602 μg/L. These compounds are described as fruity or floral (18). Among these esters, ethyl hexanoate, ethyl benzoate, ethyl octanoate, ethyl decanoate, and ethyl laurate were also present in the 2 orange wines, while the other 2 esters isoamyl acetate and diethyl succinate were only found in wines without peel contact. This suggests that most of the esters could be formed during fermentation without regard to the presence of pulp or peels.

With regard to alcohols, 2-phenylethanol was found the only common compound presented in the 2 orange wines, as well as the control wine. 1-Pentanol, (E)-3-hexen-1-ol, 1-hexanol, 1-heptanol, and 1-octanol presented only in peel contact wine, while 2-ethylhexanol was found in without peel contact wines and absent in other wines.

No aldehydes were identified in peel contact and control wine, while benzaldehyde and 2-phenylacetaldehyde were the 2 aldehydes found in wines without peel contact. Benzaldehyde has a bitter almond odor, and it is reported that the presence of benzaldehyde in wines probably formed by the oxidation of the benzyl alcohol or the effect of the microorganisms on the aromatic amino acids or on some secondary compounds such as phenyl acetic acid and *p*-hydroxybenzoic acid (29).

Hexanoic acid was found in all the 3 wines. However, octanoic acid was identified only in the control wine.

In conclusion, this study highlighted the effect of peel contact treatment on the flavor of the orange wines. Statistical analysis showed no significant differences ($p>0.05$) on the mean scores of each sensory descriptor, whereas a distinct difference was perceived on the total aroma of the wines produced with and without peel contact. The peel contact wine showed a more citrus-like and fruity aroma than the other 2 wines. It's in agreement with the results of the GC-MS that great differences were found between the wines produced with and without peel contact. In other words, peel contact treatment could be more suitable for producing orange wines due to its effect on the enhancement of the aroma of orange wines.

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