JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Effect of Oxygen on Volatile and Sensory Characteristics of Cabernet Sauvignon during Secondary Shelf Life

Dong-Hyun Lee, Bo-Sik Kang,*,† and Hyun-Jin Park*,†

School of Life Science and Biotechnology, Korea University, 5-1, Anam-dong, Sungbuk-gu, Seoul 136-701, Republic of Korea

ABSTRACT: The oxidation of Cabernet Sauvignon wines during secondary shelf life was studied by headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography−quadrupole mass spectrometry (GC−qMS) and sensory tests, with the support of multivariate statistical analyses such as OPLS-DA loading plot and PCA score plot. Four different oxidation conditions were established during a 1-week secondary shelf life. Samples collected on a regular basis were analyzed to determine the changes of volatile chemicals, with sensory characteristics evaluated through pattern recognition models. During secondary shelf life the separation among collected samples depended on the degree of oxidation in wine. Isoamyl acetate, ethyl decanoate, nonanoic acid, *n*-decanoic acid, undecanoic acid, 2-furancarboxylic acid, dodecanoic acid, and phenylacetaldehyde were determined to be associated with the oxidation of the wine. PCA sensory evaluation revealed that least oxidized wine and fresh wine was well-separated from more oxidized wines, demonstrating that sensory characteristics of less oxidized wines tend toward "fruity", "citrous", and "sweetness", while those of more oxidized wines are positively correlated with "animal", "bitterness", and "dairy". The study also demonstrates that OPLS-DA and PCA are very useful statistical tools for the understanding of wine oxidation.

KEYWORDS: red wine oxidation, secondary shelf life, Cabernet Sauvignon, OPLS-DA, PCA, volatile compounds

INTRODUCTION

Oxidation of wine is a major biochemical reaction that can greatly affect the organoleptic characteristics of wine in the (secondary) shelf life, as well as in the winemaking process.[1−3] The specific alterations can affect a wine positively or negatively, depending on the wine type. Much research has been devoted to lessen the negative deterioration of wine quality and to improve or preserve desirable sensory qualities of wine.[4−8] During winemaking, it is difficult to avoid oxygen-related problems, from prefermentation steps, such as crushing, pressing, piping, and racking of must, to postfermentation steps, such as wood barrel or stainless steel storage, filtration, and bottle filling. Additionally, the choice of stopper can dictate the degree of oxygen (O_2) permeation into the bottle, which can alter sensory properties of individual wine during secondary shelf life.[9−11] The oxidative degradation of wine aroma is dependent on several factors, including the concentration of dissolved O_2, pH, storage temperature, concentration, and types of phenolic compounds, as well as the presence of exogenous antioxidants such as sulfur dioxide (SO_2) and ascorbic acid.[12] The sensory characters associated with wine oxidation originate with paper, cardboard, cider, cooked vegetables, rancid or rotten food, and woody or pungent notes, while the presence of impact odorants of oxidized wine has been attributed to compounds such as 2,4,5-trimethyldioxolane, methional (methylthiopropanal), sotolon (3-hydroxy-4,5-dimethyl-2(5*H*)-furanone), eugenol (4-propenyl-2-methoxyphenol), 1-octen-3-ol, *t*-2-octenal, *t*-2-nonenal, furfural, 5-methylfurfural, benzaldehyde, 2-butoxyethanol, acetovanillone, and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN).[13−16] In white wines, phenolics undergo nonenzymatic oxidation in the presence of O_2, yielding polymerized polyphenols that finally precipitate in the form of brown pigments and lead to a loss of their sensorial qualities.[4] Therefore, winemakers should try to minimize contact with O_2 during the overall winemaking process to preserve sensory qualities such as fruity and fresh aromas, pale color, and acidic taste in a good condition. But, although it appears possible for white wines to develop in the bottle in the absence of O_2, undesirable reduced characters may develop if the wine's redox potential is too low as a result of too little O_2 exposure after bottling.[17] On the contrary, in red wine the addition of small and controlled amounts of O_2 enhances the development of fruity flavours, integrates the aroma of the wood, and reduces the reductive and vegetal properties (since O_2 can oxidize unwanted sulfur compounds such as hydrogen sulfide (H_2S), which has a rotten egg smell).[18] Wine oxidation involves reactions between atmospheric O_2 and various substances in wine such as phenolics, aldehydes, sugars, and H_2S, and too great an O_2 flow may cause a large negative effect in wine quality, as this can lead to the oxidation of aromas, precipitation of high-molecular-weight polymers, and browning.[19,20] However, few papers have been published on these topics, and most focus on the influence of O_2 on phenolic compounds in wine,[7,21−26] with other a few studies having focused on sensorial properties, mainly color.[27,28] Very few papers have been published on the effect of oxidation as well as microoxygenation (the application of small, continuous and controlled amounts of O_2)[18] on the volatile composition of wine during the preparation process or bottle storage, or especially secondary shelf life, which covers all the period from opening the wine stopper by the end-consumer to keeping the rest in a cellar. After the wine stopper is opened, the quality of the corresponding wine can be affected by potential

Received: March 8, 2011
Accepted: September 28, 2011
Revised: August 8, 2011
Published: September 28, 2011

dx.doi.org/10.1021/jf200759d | *J. Agric. Food Chem.* 2011, 59, 11657–11666

temperature abuse and oxygen ingress or remaining oxygen in a bottle, which may accelerate to alter wine quality in some way.

For this reason, the principal aim of this work was to evaluate the influence of O_2 on the volatile composition and organoleptic characteristics of Cabernet Sauvignon wine during a 1-week storage period with O_2 inside individual bottles being removed by O_2 scavenger or vacuum stopper, which were employed to improve the secondary shelf life, using pattern recognition models such as orthogonal projections to latent structure discriminant analysis (OPLS-DA) and principal component analysis (PCA).

MATERIALS AND METHODS

Chemicals. All chemical reagents were of analytical grade. Iron powder (200−325 mesh) and activated carbon (48−100 mesh) used in making an O_2 scavenger were purchased from Kento Chemical (Tokyo, Japan) and Sigma-Aldrich (St. Louis, MO, USA), respectively. Commercial O_2 scavenger, marketed in the form of a sachet, and laminated film (NY15 μm/PE 25 μm/COPE 60 μm) for self-made O_2 scavenger were provided from TPG (Kimpo, Korea).

Wine. Wine used in this study was produced from *Vitis vinifera* var. Cabernet Sauvignon, a representative variety of red wine, grown in the Colchagua Valley in Chile during 2004 vintage following standard winemaking procedures and wood contact of 2 years. Sample wine was selected on the basis of total polyphenol content ranging from 1.8 to 2.2 g/L holding antioxidant activity at a medium level.

O_2 Scavenger Sachets. Two O_2 scavengers were used in the study. One was an iron-based O_2 scavenger that was commercially available locally. The other was an O_2 scavenger manufactured in the biopolymer engineering laboratory, School of Life Science, Korea University, to improve O_2 absorption capacity/rate in other studies. The latter scavenger was composed of 1 g of iron powder (200−325 mesh), 1 g of activated carbon (48−100 mesh), 0.5 mL of NaCl (0.68 mol), and laminated film in NY15 μm/PE 25 μm/COPE 60 μm.

Four Storage Conditions of Secondary Shelf Life. All bottles of wine for the corresponding experiment were poured into a 20 L glass carboy to minimize quality deviation in individual bottles of wine. Transparent bottles of 750 mL were each filled with 300 mL of the pooled wine prior to capping with a stopper with or without an O_2 scavenger. Each bottle was wrapped with aluminum foil to block out light. In preparation for headspace O_2 analysis and easy sampling for analyzing volatile compounds, a 1 cm deep hole with a silicon septum projecting out of the upper side of the bottle was made with care. The headspace volume of all wine bottles was always the same, and wine samples were collected for analysis on days 1, 3, 5, and 7 since storage in a darkened wine cellar at 18 °C . Figure 1 reveals the storage conditions for each wine, where wine 1 was capped with natural cork alone, wine 2 was capped with natural cork and O_2 scavenger of low absorption capacity for oxygen, wine 3 was capped with natural cork and O_2 scavenger of high absorption capacity for oxygen, and wine 4 was capped with vacuum stopper alone. The number of bottles analyzed for each storage condition for headspace solid-phase microextraction (SPME) followed by GC−qMS analysis was 3 bottles at each time of individual storage, so that 48 bottles in total were applied in this experiment. For the accurate analysis, the experiment was performed divided into 4 batches where 1 batch equals 12 bottles in each storage condition.

In addition, we considered as "fresh wine" a product against the oxidized wines such as wine 1, wine 2, wine 3, and wine 4. The term of fresh wine was defined as just-opened, then pooled wine with no contact of O_2 since then.

Head-Space O_2 Analysis. Headspace O_2 concentration was monitored using a model 5890 gas chromatography apparatus chromatograph (Agilent, Palo Alto, CA, USA) equipped with thermal conductivity detectors and CTR-1 as column. O_2 was periodically sampled using a gas-tight syringe. O_2 analysis operating conditions were as follows: temperature of injector, oven, and detector of 50 °C, 50 °C, and 150 °C, respectively; carrier gas (helium) flow rate of 70 mL/min; injected headspace volume of 0.3 mL using a gas-tight syringe. Twelve bottles for each storage condition, where 3 bottles at each time of individual storage condition were analyzed for O_2 concentration, were applied for this experiment.

Figure 1. Photographic representation of storage conditions for each wine sample during secondary shelf life, where each condition is as follows: wine 1 under natural cork and no O_2 scavenger; wine 2 under natural cork and O_2 scavenger of low absorption capacity for oxygen; wine 3 under natural cork and O_2 scavenger of high absorption capacity for oxygen; wine 4 under vacuum stopper and no O_2 scavenger. All wines were stored totally wrapped in aluminum foil at 18 °C for 1 week.

Solid-Phase Microextraction Analysis. A headspace solid-phase microextraction (SPME) method was utilized to prepare for GC−MS analysis.[29−31] Two milliliters of each wine sample and 0.8 g of NaCl were transferred to a 20 mL headspace glass vial with a magnetic stirrer, which was then spiked with 0.4 μL of a solution containing 3-octanol (82 mg/L) and 13% ethanol as an internal standard. After testing four kinds of fibers in advance, including PDMS, CAR/PDMS, PDMS/DVB, DVB/CAR/PDMS, divinylbenzene/carboxen/polydimethylsiloxane (50/30 μm) fiber (Supelco, Bellafonte, PA, USA) with best affinity was finally applied for analysis. All vials were tightly capped with a silicon septum and pre-equilibrated for 30 min at 40 °C in a thermostatic bath with magnetic bar stirring. Afterward, the stainless steel needle positioned at the fiber housing was pushed through the vial septum, and the fiber was pushed out of the housing and exposed for 30 min at 40 °C to the headspace generated in the sample vial. After extraction, the fiber was pulled back into the housing, and the SPME device was removed from the vial and inserted into the injection port of the GC for thermal desorption of the analytes.

Volatile Compound Analysis. A model 7890 GC (Agilent Technologies) coupled to a model 5975C quadrupole mass spectrometer (Agilent Technologies) was used to analyze volatile compounds with a DB-WAX bonded fused capillary column (30 m × 0.32 mm internal diameter × 0.25 μm; J&W Scientific, Folsom, CA, USA) being employed. The analyses were performed at an inlet temperature of 250 °C; splitless time of 1 min; purge flow rate to the split vent of 50 mL/min for 1 min; column head pressure of 14.14 psi; a helium carrier gas flow rate of 1.0 mL/min; and an average helium gas velocity of 25 cm/s. The oven temperature was held at 40 °C for 4 min, increased from 40 to 80 °C in an increment of 2.5 °C/min, from 80 to 110 °C in an increment 5 °C/min, and from 110 to 220 °C in an increment of 10 °C/min, and held for 5 min at 220 °C. Quadrupole mass spectrometry (qMS) was conducted in electron impact (EI) mode at 70 eV, and data acquisition

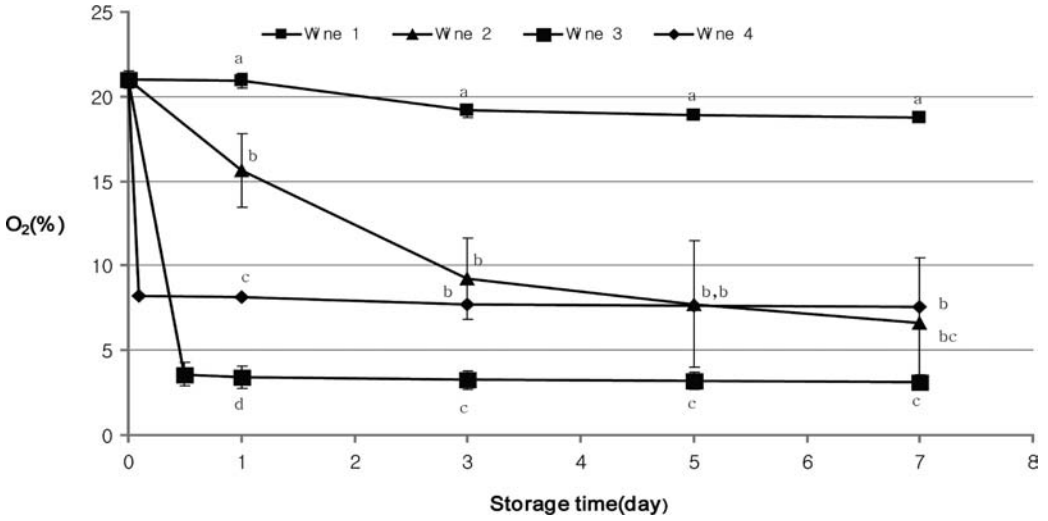

Figure 2. O_2 levels in each wine bottle stored during secondary shelf life. Error bars are the standard mean error. O_2 concentratrion was expressed as mean ± SD (n = 3). Means of O_2 level at each time point with different letters are significantly different, $p < 0.05$.

was performed in full scan mode for 50−650 m/z with a scan time of 2.9 s. Selected GC−qMS peaks were identified by comparing the mass spectra with those from both the National Institute of Standards and Technology (NIST) and Wiley registry. To quantify the volatiles, each sample prepared in triplicate was run in two different injections, and the integrated area based on the total ion chromatograms was naturalized to the area of the internal standard (3-octanol) and averaged. All samples obtained at specified collection times from wine 1, wine 2, wine 3, wine 4, and fresh wine were analyzed, and the resulting data were analyzed in the appropriate statistical methods such as ANOVA, OPLS, and PCA, but not all data are shown in the article.

Sensory Analysis. The sensory panelists comprised eight judges aged 27−50 years. All of the judges had extensive experience in sensory analysis and had been working for the Wine Academy of KangNam. Judges were trained during three 1-h sessions. In sessions one and two, the two different aroma standards and aroma kit solely patented and developed by the Wine Academy of KangNam were presented and discussed. From these panelist discussions, nine aroma terms (fruity, citrous, woody, spicy, mushroom, green, dairy, animal, overall flavor) that best captured wine oxidation and five taste terms (sourness, sweetness, bitterness, astringency, overall taste) including mouth-feel attributes were selected by panelist consensus. In training session three, the panelists scored the intensity of each attribute in four oxidized wines on a 7-point scale where just-opened fresh wine provided the reference point score of 4 (1 = lowest, 2 = lower, 3 = low, 4 = same, 5 = high, 6 = higher, 7 = highest). In all cases, samples (20 mL) were served in black tulip-shaped wine glasses, which were identified by a randomly generated 3-digit number, and covered with a Petri-dish top after an equilibration time of 20 min at 21 °C.

Statistical Analyses. Statistical analysis of the data such as volatile and descriptive analyses was carried out by analysis of the variance (ANOVA) and Duncan's multiple-range using SPSS version 12.0 (SPSS, Chicago, IL, USA). The resulting data sets from GC−qMS and sensory evaluation were processed in the support of SIMCA-P (Soft Independence Modeling of Class Analogy) version 12.0 (Umetrics, Umeå, Sweden) for multivariate data analysis. A supervised pattern recognition method, OPLS-DA, was performed to extract maximum information on discriminant compounds or to maximize the separation between samples from GC−qMS data sets. OPLS-DA can be described as the regression extension of PCA that gives the maximum covariance between measured data and the response variable. The quality of the models using OPLS-DA is described by R^2x and Q^2 values. R^2x is defined as the proportion of variance in the data explained by the models and indicates goodness of fit. Q^2 is defined as the proportion of variance in the data predicted by the model and indicates predictability.[32,33] PCA, an unsupervised pattern recognition method, was employed to reduce the dimensionality of the original data matrix retaining the maximum amount of variability in sensory evaluation and to visualize the correlation between the intensity ratings by panelists for the attributes for each "oxidized wine" and corresponding oxidized wine samples.

RESULTS AND DISCUSSION

Level of O_2 Concentration in Four Wines with Storage Time. The overall pattern for the level of oxygen concentration in four wines with storage time, respectively, is shown in Figure 2. In general, oxygen concentration in all wines decreased with time, and among them, the level of oxygen in wine 3 decreased drastically from initial storage time. On day 1 of storage, its O_2 concentration reached around 3%, continuing to the end as it is. As for wine 4, it had a similar behavior compared to wine 3, but the level of O_2 was maintained at around 7% to the end. On the other hand, the O_2 level in wine 2 decreased slowly to about 9% after 3 days and then decreased very little, while wine 1 decreased gradually to around 19%, remaining constant to the end.

OPLS-DA Pattern of Volatile Compounds during Storage for Each Wine. To provide comparative interpretation for volatile chemical changes in each wine, the OPLS-DA pattern recognition method was applied to the GC−MS data to visualize the development of volatile compounds and the differentiation of wine samples according to storage time. OPLS-DA score plot of wine 1, which was the most oxidized of the four wines, showed a clear differentiation between samples collected from wine 1 with storage time, demonstrating a good fitness and high predictability of the OPLS-DA model with high statistical values of R^2x (0.89), R^2y (0.92), and Q^2 (0.73) (Figure 3A). Counterclockwise rotation of the plot indicated a change of volatile compounds in wine 1 capped with natural cork only during the 7-day oxidation period. The loading plot provided information of the volatile compounds that contributed to the separation and revealed significant differences between ethyl acetate, isoamly acetate, methyl hexanoate, isoamyl alcohol, ethyl hexanoate, 1-hexanol, ethyl octanoate, 16-hydroxyhexadecanoic acid, furfural, ethyl

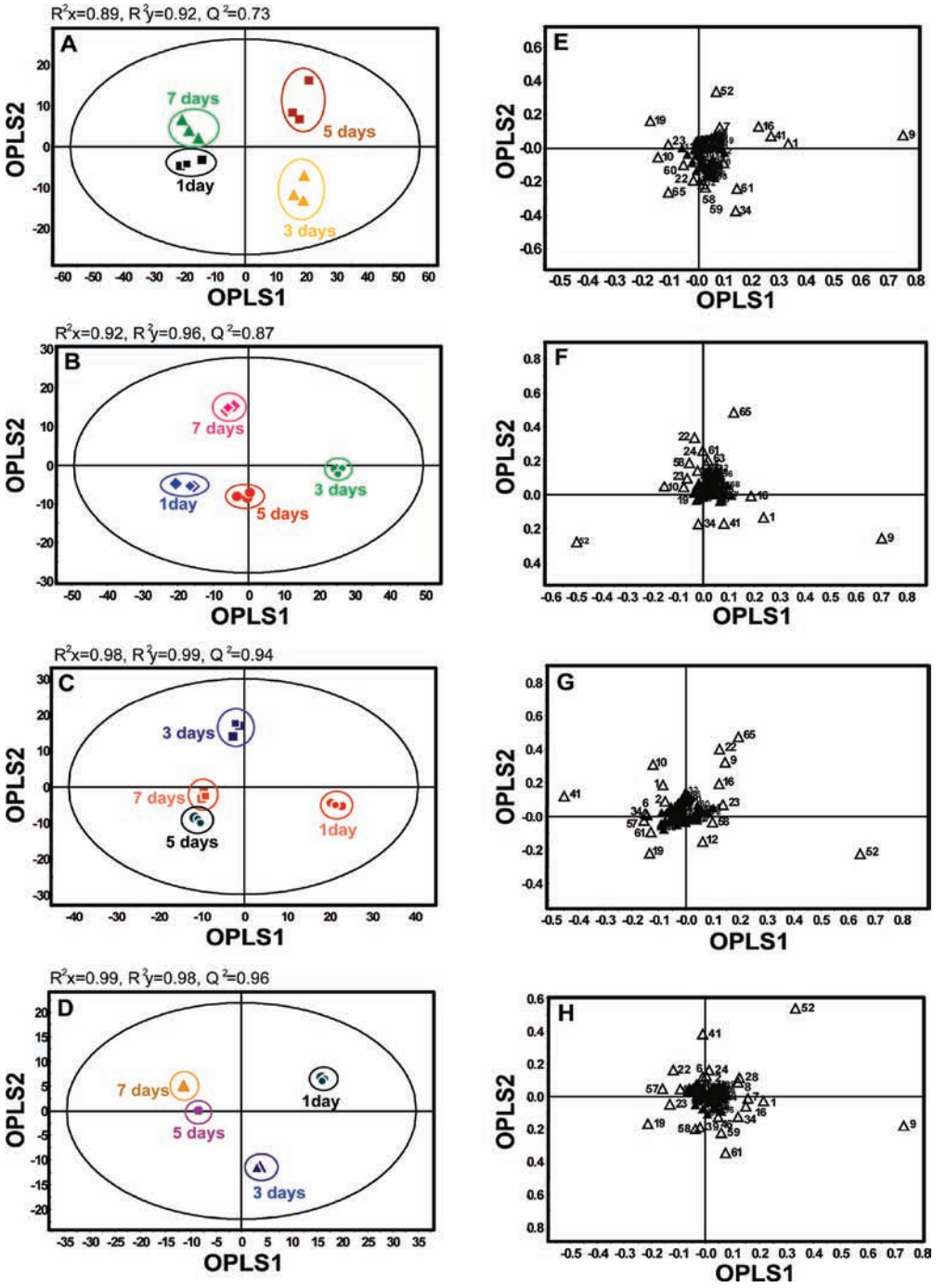

Figure 3. The OPLS-DA score (A−D) and loading (E−H) plots derived from volatile compounds on GC−MS of each wine being stored for seven days: wine 1 (A, E); wine 2 (B, F); wine 3 (C, G); wine 4 (D, H). Volatile compounds with open symbols are significantly different by Duncan's multiple-range test at $p < 0.05$.

decanoate, diethyl succinate, phenylethyl alcohol, nonanoic acid, 4-ethylphenol, *n*-decanoic acid, 2-methyl-5-(1-methylethyl)-phenol, and ethyl hydrogen succinate by Duncan's multiple range test at $p < 0.05$ (Figure 3E and Table 1).

Figures 3B−3D depict the OPLS-DA score plots of the other three wines, providing comparisons with high values of R^2x, R^2y, Q^2, respectively. The score plot of wine 2 (Figure 3B), which was the second most oxidized of the four wines, revealed that the separation among samples collected from wine 2 with storage time on the OPLS-DA plane was very similar to that of wine 1, although it did not demonstrate the same counterclockwise movement according to the increase in storage time, as did the score plot of wine 1. By component 1, the fact that the two samples collected on day 1 and day 3 were well-separated, while samples obtained on day 5 and day 7 were less separated, was related reasonably well with the results from Figure 2, where the O_2 level of wine 2 during the first 3 days decreased greatly, while decreasing only marginally thereafter. The volatile compounds such as ethyl acetate, isoamyl alcohol, ethyl hexanoate, 3-methyl-1-pentanol, 1-hexanol, ethyl octanoate, 16-hydroxyhexadecanoic

Table 1. Volatile Compounds Significantly Different at $p < 0.05$ in Each Wine during Secondary Shelf Life of 1 Week

volatile compounds	wine 1	wine 2	wine 3	wine 4
ethyl acetate	◎	◎	◎	◎
ethyl propanoate			◎	
2-methyl-1-propanol			◎	◎
isoamyl acetate	◎			◎
methyl hexanoate	◎			◎
isoamyl alcohol	◎	◎	◎	◎
ethyl hexanoate	◎	◎	◎	
2-*n*-butylfuran			◎	◎
3-methyl-1-pentanol		◎		
1-hexanol	◎	◎	◎	◎
ethyl octanoate	◎	◎	◎	◎
16-hydroxyhexadecanoic acid	◎	◎	◎	◎
furfural	◎	◎	◎	◎
2-ethyl-1-hexanol				◎
ethyl nonanoate				◎
ethyl decanoate	◎	◎	◎	◎
1-nonanol				◎
diethyl succinate	◎	◎	◎	◎
2-phenylethyl acetate				◎
phenylethyl alcohol	◎	◎	◎	◎
octanoic acid			◎	◎
nonanoic acid	◎	◎	◎	◎
4-ethylphenol	◎			◎
2-methyl-5-(1-methylethyl)phenol	◎			
n-decanoic acid	◎	◎	◎	◎
ethyl hydrogen succinate	◎	◎	◎	
dodecanoic acid				◎

acid, furfural, ethyl decanoate, diethyl succinate, phenylethyl alcohol, nonanoic acid, *n*-decanoic acid, and ethyl hydrogen succinate contributed to this separation (Figure 3F and Table 1).

The score plot of wine 3 (Figure 3C), which was the least oxidized wine, displayed very poor separation according to storage time, compared with that of wine 1 and wine 2. By the criterion of component 1, the sample from day 1 to the right side in the OPLS-DA score plot was well-separated from three samples obtained from days 3, 5, and 7 to the left side in the score plot. The corresponding loading plots showed that the following compounds contributed to the separation: ethyl acetate, ethyl propanoate, 2-methyl-1-propanol, isoamyl alcohol, ethyl hexanoate, 2-*n*-butylfuran, 1-hexanol, ethyl octanoate, 16-hydroxyhexadecanoic acid, furfural, ethyl decanoate, diethyl succinate, phenylethyl alcohol, octanoic acid, nonanoic acid, *n*-decanoic acid, and ethyl hydrogen succinate (Figure 3G and Table 1).

The score plot of wine 4, which was capped with vacuum stopper and was the third most-oxidized wine, was very similar to that of wine 3, which was the least oxidized (Figure 3D), suggesting that the four samples were divided into three groups by first component of the OPLS-DA score plot, where one group is

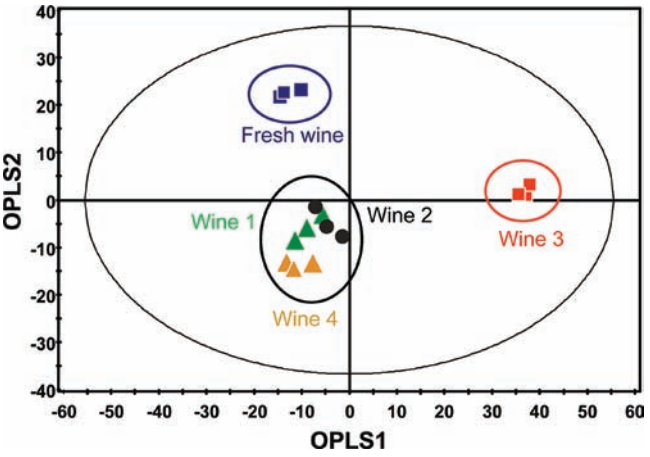

Figure 4. The OPLS-DA score plot of the samples collected from each wine on day 7 from storage and fresh wine, which is just-opened, then pooled wine with no contact of O_2 since then.

for samples from day 1, another for samples from day 3, the other for samples from day 5 and day 7. The volatile compounds responsible for the separation in the score plot were as follows by the corresponding loading plot (Figure 3H and Table 1): ethyl acetate, 2-methyl-1-propanol, isoamyl acetate, methyl hexanoate, isoamyl alcohol, 2-*n*-butylfuran, 1-hexanol, ethyl octanoate, 16- hydroxyhexadecanoic acid, furfural, 2-ethyl-1-hexanol, ethyl nonanoate, ethyl decanoate, 1-nonanol, diethyl succinate, 2-phenylethyl acetate, phenylethyl alcohol, octanoic acid, nonanoic acid, 4-ethylphenol, *n*-decanoic acid, and dodecanoic acid.

To obtain more specific results associated with wine oxidation, the OPLS-DA score plot including the GC−MS data of fresh wine as well as that of four oxidized wines collected on day 7 since storage has been created. The plot showed a clear separation with high values of R^2x (0.93), R^2y (0.96), and Q^2 (0.85) (Figure 4). The score plot showed that all wines were well-separated in three groups, demonstrating that one group comprised fresh wine, another group the least oxidized wine (wine 3), and the remaining group more oxidized wines (wine 1, wine 2, and wine 4) than fresh wine and wine 3 already mentioned. In an effort to identify volatile chemicals involved in these oxidation phenomena with certainty, three samples obtained from fresh wine, wine 1, and wine 3 as representative of the three aforementioned groups were used for a one-way ANOVA. Phenylethyl alcohol, ethyl acetate, isoamyl acetate, ethyl hexanoate, ethyl decanoate, nonanoic acid, *n*-decanoic acid, undecanoic acid, 2-furancarboxylic acid, dodecanoic acid, and phenylacetaldehyde were significantly different by Duncan's multiple range test at $p < 0.001$ (Table 2).

Volatile Compounds Related to the Oxidation of a Cabernet Sauvignon. Judging from the results of Table 2, eight volatile chemicals (isoamyl acetate, ethyl decanoate, nonanoic acid, *n*-decanoic acid, undecanoic acid, 2-furancarboxylic acid, dodecanoic acid, and phenylacetaldehyde) were considered to have a possibility of a positive or negative correlation with the degree of oxidation of a Carbernet Sauvignon, while three volatile chemicals, namely, phenylethyl alcohol, ethyl acetate, and ethyl hexanoate, did not show such a logical consistency with degree of oxidation, so that more research should be needed.

Isoamyl acetate is a typical type of fusel alcohol acetate with banana notes.[34] The basic odor of wines has been attributed to four esters including isoamyl acetate as well as ethyl acetate, ethyl

Table 2. Volatile Compounds in Fresh Wine, Wine 1, and Wine 3 at the 7th Day during Secondary Shelf Life[a]

				storage conditions		
no.	volatile compds[b]	odor descriptor	t_R (minutes)	fresh wine	wine 1	wine 3
		Higher Alcohol				
1	2-methyl-1-propanol*	bitter	9.36	4.3 b	4.9 b	10.2 a
2	isoamyl alcohol*	fusel	14.78	364.4 b	332.4 b	929.7 a
3	3-methyl-1-pentanol*		20.37	1.0 b	2.3 a	1.4 b
4	1-hexanol*	green grass	21.61	42.4 b	40.9 b	80.6 a
5	3-hexen-1-ol*	grass	22.07	1.3 b	1.1 b	2.5 a
6	1-nonen-3-ol		25.32	0.8	0.9	0.6
7	heptanol*		25.46	1.7 b	2.0 b	2.6 a
8	2-ethyl-1-hexanol**		26.56	6.4 b	2.9 c	10.8 a
9	3-ethyl-4-methylpentanol*		27.07	0.9 b	0.8 b	1.4 a
10	1-octanol*		28.23	2.7 b	4.1 b	7.7 a
11	1-hexen-3-ol*		28.73	12.6 a	7.9 b	13.5 a
12	1-nonanol*		29.87	4.8 a	3.2 b	5.0 a
13	4-trimethyl-3-cyclohexene-1-methanol*		30.35	5.9 a	4.6 b	7.3 a
14	benzyl alcohol		32.39	3.2	3.3	3.6
15	**phenylethyl alcohol*** **	**rose**	**32.75**	**518.6 a**	**230.2 b**	**199.3 c**
16	2-furanmethanol*		30.00	2.2 b	3.1 ab	4.0 a
		Ester				
17	**ethyl acetate*** **	**ethereal-fruity**	**3.26**	**54.4 b**	**33.6 c**	**117.5 a**
18	ethyl propanoate*	sweet, fruity	4.65	2.7 b	2.1 b	5.7 a
19	ethty 2-methyl propanoate*	sweet, fruity	4.79	2.6 b	3.0 b	4.7 a
20	ethyl butanoate**	fruity, sweet	6.75	3.7 c	4.7 b	7.1 a
21	ethyl 3-methyl-butanoate*	fruity, floral	7.85	1.8 b	5.0 a	5.9 a
22	**isoamyl acetate*** **	**banana**	**9.88**	**12.9 c**	**19.4 a**	**16.0 b**
23	methyl hexanoate*		12.62	0.8 b	1.4 a	0.9 b
24	**ethyl hexanoate*** **	**fruity**	**14.95**	**97.0 a**	**75.7 b**	**7.7 c**
25	hexyl acetate	fruity, herb	17.01	1.0	0.7	0.8
26	ethyl heptanoate		20.09	1.0	0.7	1.3
27	ethyl 2-hexenoate		20.73	1.2	1.2	1.6
28	methyl octanoate		22.71	1.2	1.4	1.1
29	ethyl octanoate**	ripe fruit	24.46	75.4 a	68.8 a	47.8 b
30	ethyl nonanoate*		27.59	1.8 b	1.3 b	3.1 a
31	ethyl 3-(methylthio)propanoate*		28.40	2.2 ab	1.5 b	2.8 a
32	**ethyl decanoate*** **	**fruity**	**29.52**	**51.8 a**	**24.6 c**	**36.1 b**
33	ethylmethyl ester*		29.60	3.1 ab	2.7 b	3.4 a
34	diethyl succinate*	fermented, floral	30.13	182.7 b	169.1 b	227.1 a
35	methyl 2-hydroxy- benzoate**		31.27	1.5 b	1.1 c	2.3 a
36	diethyl pentanedioate*		31.31	7.8 a	4.3 b	8.0 a
37	ethyl benzeneacetate*		31.37	5.3 a	3.8 b	5.2 a
38	2-phenylethyl acetate*		31.69	13.5 a	10.7 b	13.2 a
39	1-methylethyl dodecanoate*		31.76	8.4 a	2.4 b	7.1 a
40	ethyl dodecanoate*		31.87	5.8 a	2.9 b	6.7 a
41	2-ethyl hexanoate*		33.12	1.3 a	0.7 b	1.2 a
42	diethyl hydroxybutanedioate		34.03	8.0	5.9	7.6
43	diethyl phthalate		37.06	4.2	5.1	4.9
44	ethyl hydrogen succinate		37.19	46.7	53.5	40.5
45	propyl pentanoate		38.28	2.0	2.1	3.1
46	dibutyl phthalate*		40.88	4.0 a	1.6 b	3.2 a
		Acid				
47	16-hydroxyhexadecanoic acid**		25.81	16.2 a	24.5 ab	36.2 a
48	butanoic acid		29.64	1.2	1.2	2.2

Table 2. Continued

				storage conditions		
no.	volatile compds[b]	odor descriptor	t_R (minutes)	fresh wine	wine 1	wine 3
49	heptanoic acid	floral	29.64	4.0	3.9	5.4
50	hexanoic acid*	pineapple	32.07	14.3 b	13.1 b	20.9 a
51	octanoic acid	rotten fruit	34.21	22.4	22.5	24.3
52	**nonanoic acid*** **	**rancid**	**35.21**	**6.8 a**	**3.1 c**	**4.7 b**
53	***n*-decanoic acid *** **	**fatty, sour**	**36.17**	**53.3 a**	**26.1 c**	**34.4 b**
54	**undecanoic acid*** **		**37.09**	**7.5 a**	**1.4 c**	**4.1 b**
55	benzenecarboxylic acid *		37.76	4.5 ab	3.6 b	5.7 a
56	**2-furancarboxylic acid *** **		**37.93**	**5.9 a**	**2.7 b**	**4.7 ab**
57	**dodecanoic acid *** **	**soap**	**38.10**	**6.7 a**	**3.9 c**	**5.1 b**
		Aldehyde				
58	benzaldehyde*		27.38	1.6 b	0.9 b	3.7 a
59	**phenylacetaldehyde*** **	**flowery, rose**	**29.73**	**0.9 c**	**2.6 a**	**1.7 b**
60	furfural*	sweet, bread-like	25.83	30.7 b	32.1 b	37.7 a
61	5-methyl-2-furancarboxaldehyde		28.59	2.7	2.9	3.2
62	5-(hydroxymethyl)-2-Furancarboxaldehyde*		38.43	3.0 a	1.8 b	3.9 a
		Miscellaneous				
63	phenol		33.76	0.6	0.7	0.9
64	4-ethyl-2-methoxy-phenol*		33.95	8.4 a	5.4 b	7.6 a
65	4-ethylphenol*	phenolic, leather	35.36	19.6 a	14.5 b	14.3 b
66	2-methyl-5-(1-methylethyl)-phenol		35.40	3.1	3.6	2.9
67	2,5-bis(1,1-dimethylethyl)-phenol*		36.50	5.3 a	1.4 c	3.0 b
68	2-*n*-butylfuran *		18.15	17.2 b	16.7 b	18.6 a
69	1-(2-furanyl)-ethanone*		26.99	1.8 b	1.4 b	2.6 a
70	5-butyldihydro-4-methyl-2-furanone*		32.47	5.5 a	3.7 b	5.7 a
71	2,3-dihydrobenzofuran		37.34	4.8	5.0	4.8
72	ethyl 2-furancarboxylate*		29.43	3.5 b	3.0 b	7.5 a

[a] Values with different letters are significantly different by Duncan's multiple-range test at ***$p < 0.001$, **$p < 0.01$, and *$p < 0.05$. Volatile compounds significantly different at $p < 0.001$ are in bold. [b] Volatile compounds measured in ppm.

hexanoate, and ethyl octanoate, all of which are fermentation products.[35] The result in Table 2 shows that isoamyl acetate increased with higher oxidation level, being highest in the most oxidized wine (wine 1). This result was different from that of a previous study[36] reporting that isoamyl acetate slowly decreased to make isoamyl alcohol and ethanol by hydrolysis during oxidative aging. On the contrary, however, another study reported the increase of isoamyl acetate after 20 weeks in wood, which may have been related to a change in the equilibrium for increasing levels of acetic acid and the high concentration of isoamyl alcohol.[37]

Ethyl decanoate, which is a typical ethyl ester of a long chain fatty acid (C_{10}) with a pleasant or fruity note,[38] is produced during yeast fermentation by the reactions of ethanol and acyl-coenzyme A derivatives.[39] Our results showed that ethyl decanoate decreased with higher oxidation level (Table 2), providing its lowest concentration in the most oxidized wine 1, and this result corresponded to other experiments. Other studies have reported ethyl decanoate increased before malo-lactic fermentation while decreasing after that process, and, compared with other ethyl esters, ethyl decanoate hydrolyzed so rapidly to become decanoic acid and ethanol with oxidative storage time that it was often undetectable after long periods.[18,40] In addition, while most ethyl esters exhibit inconsistency in their levels according to storage time and aging matrix, such as wood barrel or bottle, ethyl decanoate consistently decreased in a way that is unrelated to the two aforementioned factors.[36]

Nonanoic acid (C_9), decanoic acid (C_{10}), undecanoic acid (C_{11}), and dodecanoic acid (C_{12}) are typical types of medium and long chain (9−12 carbons) fatty acids in oxidized wine with fatty, rancid, and soap notes.[34,38,41] This study showed the four long chain fatty acids mentioned above were decreased as the oxidation level of the wine increased (Table 2). In general, microoxygenation treatment enhanced the presence of fatty acids, and this could be related to a higher hydrolysis of their corresponding ester or even to a low initial formation of esters. However, if a qualitative correlation could be detected, it is not possible to establish a quantitative correlation between changes in ethyl ester and fatty acids levels.[18] On the other hand, a study conducted with Madeira wines reported a significant decrease in medium chain and some long chain fatty acids, namely, hexanoic acid and octanoic acid during conservation, with the exception of decanoic acid whose concentration decreased slightly, while short chain fatty acids, particularly butanoic acid and isobutanoic acid, increased their contents during wine aging.[39]

2-Furancarboxylic acid, also known as 2-furonic acid, is produced by oxidation of the aldehyde group of 2-furfural with sweet and bread-like notes.[38] In this study, furfural had no significant difference in its concentration between fresh wine and wine 1, while 2-furancarboxylic acid showed a decreasing

Table 3. Mean of Sensory Note Ratings of the Wines at the 7th Day since Secondary Shelf Life[a,b]

sensory notes	fresh wine	wine 1	wine 2	wine 3	wine 4
furity*	**4.0 ab**	**3.1 c**	**3.4 abc**	**4.2 a**	**3.3 bc**
citrous	4.0 a	3.1 b	3.7 ab	4.1 a	3.6 ab
woody*	**4.0 a**	**2.9 b**	**3.8 a**	**4.1 a**	**4.1 a**
spicy	4.0	3.4	3.5	3.8	3.8
mushroom	4.0	4.1	4.1	4.2	4.8
green grassy	4.0	4.0	3.9	4.3	4.5
dairy	4.0	4.1	4.0	3.9	4.2
animal*	**4.0 b**	**5.1 a**	**4.1 b**	**3.6 b**	**4.3 ab**
overall flavor**	**4.0 a**	**2.3 b**	**3.3 a**	**4.1 a**	**3.7 a**
sourness	4.0	4.4	3.9	3.5	4.2
bitterness	4.0 ab	4.1 ab	4.0 ab	3.8 b	4.7 a
astringency	4.0	4.4	4.1	3.5	4.3
sweetness*	**4.0 a**	**3.1 b**	**3.7 ab**	**3.9 a**	**3.4 ab**
overall taste**	**4.0 a**	**2.8 c**	**3.1 bc**	**3.8 ab**	**3.1 bc**
overall mouthfeel*	**4.0 a**	**2.8 b**	**3.2 b**	**3.5 ab**	**3.1 b**

[a] Values with different letters in lowercase are significantly different by Duncan's multiple-range test at $^{**}p < 0.01$, and $^{*}p < 0.05$, but values with different letters in lowercase and no asterisk in the same row are significantly different by Duncan's multiple-range test at $p < 0.1$. [b] $n = 8$ judges $\times$ 2 replications. Sensory notes significant at $^{**}p < 0.01$ and $^{*}p < 0.05$ for each wine are in bold.

behavior as the level of oxidation increased (Table 2). Furfural is mainly formed by the degradation of hemicellulose during toasting of the barrel, but in aged wines it does not originate exclusively from the oak cask, but can also be formed from the carbohydrates occurring in wines during the aging period.[36,42,43] Some authors stated[36,44−46] that furfural decreased during oxidative storage time and could be related to the fact that furfural was implicated in the aldehyde-generating reactions with flavanols or anthocyanins in wine, producing new color or more stable pigments. Therefore, the level of 2-furancarboxylic acid directly made from oxidation of 2-furfural can be also decreased with a high degree of oxidation.

Phenylacetaldehyde is produced by the oxidation of phenylethyl alcohol, which is very abundant in wine, generating notes of rose in light of organoleptic characteristics. Presently, the oxygen inside the wine bottle employed in the experiment may have been a primary cause of increase in phenylacetaldehyde, judging from the decrease of phenylethyl alcohol in both wine 1 and wine 3 over fresh wine (Table 2).

Phenylacetaldehyde is a volatile compound showing less favorable odor properties in oxidation of both red wine and white wine in several studies on wine oxidation.[14,47] Increased phenylacetaldehyde can cause a deterioration of sensory quality in an oxidized red wine and is negatively correlated with pleasant descriptors.[47] In addition, phenylacetaldehyde, together with methional, is the most impactful factor in the quality of white wine in wine oxidation, revealing the presence of a strong smelling aldehyde.[15] Gas chromatography−olfactometry and aroma extract dilution analysis of a normal wine and a spoiled wine led to the identification of substances mainly related with the typical oxidative white wine aromas such as phenylacetaldehyde as well as 3-(methylthio)propionaldehyde.[14] Therefore, the increase of phenylacetaldehyde with degree of oxidation in the present work may be correlated with the result of sensory evaluation that will be described in the next part of this work.

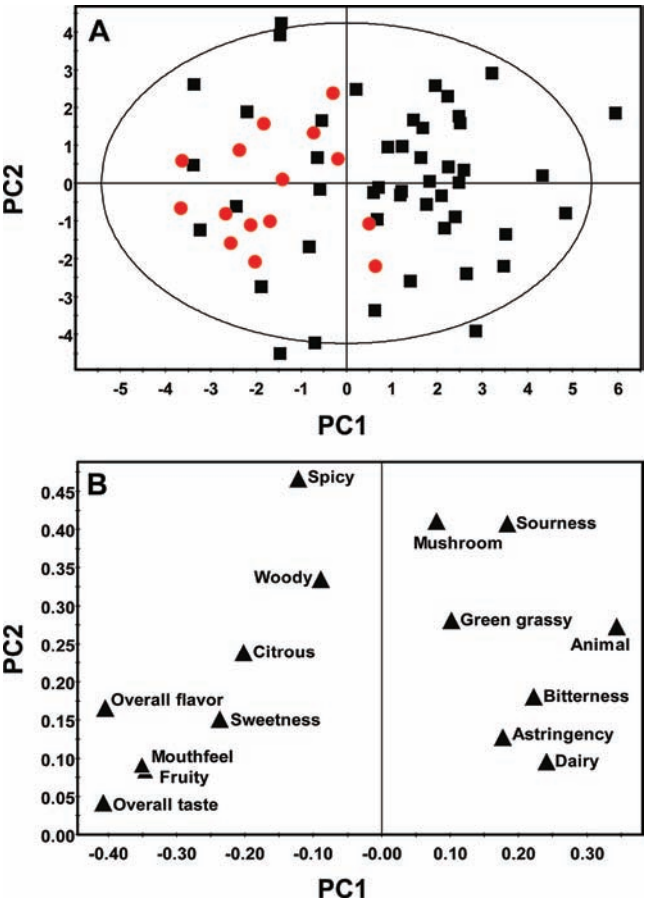

Figure 5. PCA score plot (A) and loading plot (B) of descriptive data for five wines, including fresh wine: (red ●) fresh wine and wine 3; (black ■) wine 1, wine 2, and wine 4 (PC1 and PC2 are 27% and 17% of variation, respectively; letters correspond to sensory attributes as shown in Table 3).

Sensory Evaluation. To profile the sensory characteristics of each oxidized wine, the samples were evaluated by descriptive analysis. Mean intensity ratings and Duncan's multiple-range test are given in Table 3. From the results of ANOVA conducted on the descriptive data, some aroma attributes such as "fruity", "woody", and "animal" and taste attributes such as "sweetness", including overall flavor, overall taste, and overall mouthfeel, were significantly different across the wines at $p < 0.05$ or $p < 0.01$. These sensory notes selected by the panelists did not agree with some previous descriptions. One study reported that, in the oxidation of red Grenache wines, color intensity, orange shade, animal, bitterness, and astringency notes contributed to the significant difference in the sensory quality of Grenache wine.[48] These results may be related to changes in polyphenolic composition, as previously mentioned in other studies on microoxygenation.[7,40,49,50] Moreover, the wines that have received more O_2 were perceived as being higher in fruity and caramel odor and lower in animal character. They also showed more intense and more orange color.[48] In addition, another study suggested[51] that, in young red wines from Rioja Alavesa, nine sensory attributes changed significantly through time: red berry aroma and flavor, body, balance, purple hue, and color intensity increased, whereas alcoholic aroma and flavor and astringency decreased. The results of PCA factor loading plot (biplot mode with varimax

rotation) for the sensory variables and the intensity ratings for each oxidized wine are shown in Figure 5A and Figure 5B.

The data revealed that the group consisting of both fresh wine and wine 3 was well separated from the other groups formed by wine 1, wine 2, and wine 4, with the first two principal components captured as 44% of the sample variance. In addition, the figures depict the projection of the wines in the space defined by the sensory attributes, demonstrating the clear separation of the wines in their oxidation along the first axis, where fresh wine and wine 3, the least oxidized wine, were located in the left side accompanying some sensory notes such as "fruity", "overall taste", "overall flavor", and "mouthfeel", whereas highly oxidized wines (wine 1, wine 2, and wine 4) were positioned in the right side together with the following notes: "animal", "sourness", "dairy", and "astringency".

In conclusion, this research has shown that the oxidation behavior of Cabernet Sauvignon wine during secondary shelf life can be identified in the OPLS-DA method with some volatile compounds such as isoamyl acetate, ethyl decanoate, nonanoic acid, *n*-decanoic acid, undecanoic acid, 2-furancarboxylic acid, dodecanoic acid, and phenylacetaldehyde involved in significance. Besides, with sensory evaluation followed by the PCA method, it was found that sensory notes derived from fresh wine and least oxidized wine were different from those of more oxidized wines on all occasions including flavor and taste. But it was difficult to interpret the intricateness of wine oxidation just depending on oxygen and volatile compounds. One study reported that the scores plot of oxidized wines, several red wines including Cabernet Sauvignon and Pinot noir, and the loadings plot of their volatiles through the PCA method differed to a great extent with the influence of microoxygenation treatments. One explanation for these results could be found in their diverging phenolic composition, namely, the level of flavan-3-ol and anthocyanin or their ratio and the level of catechin/epicatechin.[52] Therefore, although a good classification according to the degree of oxidation and the identification of volatiles involved were obtained by OPLS-DA or PCA, this may be the result of being investigated on volatile compounds only, so future work needs to be carried out to interpret wine oxidation with getting by far more information concerning the polyphenolic compounds that are very abundant in red wine.

AUTHOR INFORMATION

Corresponding Author

*Tel: +82-2-3290-3450. Fax: +82-2-953-5892. E-mail: hjpark@korea.ac.kr.

Author Contributions

†Both B.-S.K. and H.-J.P. equally contributed to this research as cocorresponding authors.

Funding Sources

We thank HiBio Co., Ltd. for the financial support.

ACKNOWLEDGMENT

We thank HiBio Co., Ltd., for the wine supply and Dr. Lee, Jang-Eun and Dr. Ko, Bong-Kuk for providing a lot of statistical advice.

REFERENCES

(1) Escudero, A.; Asensio, E.; Cacho, J.; Ferreira, V. Sensory and chemical changes of young white wines stored under oxygen. An assessment of the role played by aldehydes and some other important odorants. *Food Chem.* **2002**, *77*, 325–331.

(2) Fu, Y.; Lim, L. T.; McNicholas, P. D. Changes on enological parameters of white wine packaged in bag-in-box during secondary shelf life. *J. Food Sci.* **2009**, *74*, C608–C618.

(3) du Toit, W. J.; Marais, J.; Pretorius, I. S.; du Toit, M. Oxygen in must and wine: A review. *S. Afr. J. Enol. Vitic.* **2006**, *27*, 76–94.

(4) El Hosry, L.; Auezova, L.; Sakr, A.; Hajj-Moussa, E. Browning susceptibility of white wine and antioxidant effect of glutathione. *Int. J. Food Sci. Technol.* **2009**, *44* (12), 2459–2463.

(5) Gonzalez-Sanjose, M. L.; Ortega-Heras, M.; Perez-Magarino, S. Microoxygenation treatment and sensory properties of young red wines. *Food Sci. Technol. Int.* **2008**, *14*, 123–130.

(6) Atanasova, V.; Fulcrand, H.; Cheynier, V.; Moutounet, M. Effect of oxygenation on polyphenol changes occurring in the course of wine-making. *Anal. Chim. Acta* **2002**, *458*, 15–27.

(7) Sanchez-Iglesias, M.; Gonzalez-Sanjose, M. L.; Perez-Magarino, S.; Ortega-Heras, M.; Gonzalez-Huerta, C. Effect of micro-oxygenation and wood type on the phenolic composition and color of an aged red wine. *J. Agric. Food Chem.* **2009**, *57*, 11498–11509.

(8) Bradshaw, M. P.; Scollary, G. R.; Prenzler, P. D. Examination of the sulfur dioxide-ascorbic acid anti-oxidant system in a model white wine matrix. *J. Sci. Food Agric.* **2004**, *84*, 318–324.

(9) Skouroumounis, G. K.; Kwiatkowski, M. J.; Francis, I. L.; Oakey, H.; Capone, D. L.; Duncan, B.; Sefton, M. A.; Waters, E. J. The impact of closure type and storage conditions on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine during five years' storage. *Aus. J. Grape Wine Res.* **2005**, *11*, 369–377.

(10) Kwiatkowski, M. J.; Skouroumounis, G. K.; Lattey, K. A.; Waters, E. J. The impact of closures, including screw cap with three different headspace volumes, on the composition, colour and sensory properties of a Cabernet Sauvignon wine during two years storage. *Aust. J. Grape Wine Res.* **2007**, *13*, 81–94.

(11) Godden, P.; Francis, L.; Field, J.; Gishen, M.; Coulter, A.; Valente, P.; Hoj, P.; Robinson, E. Wine bottle closures: physical characteristics and effect on composition and sensory properties of a Semillon wine - 1. Performance up to 20 months post-bottling. *Aust. J. Grape Wine Res.* **2001**, *7*, 64–105.

(12) Ferreira, A. C. S.; Guedes de Pinho, P.; Rodrigues, P.; Hogg, T. Kinetics of oxidative degradation of white wines and how they are affected by selected technological parameters. *J. Agric. Food Chem.* **2002**, *50*, 5919–5924.

(13) Escudero, A.; Cacho, J.; Ferreira, V. Isolation and identification of odorants generated in wine during its oxidation: a gas chromatography-olfactometric study. *Eur. Food Res. Technol.* **2000**, *211*, 105–110.

(14) Ferreira, A. C. S.; Hogg, T.; Guedes de Pinho, P. Identification of key odorants related to the typical aroma of oxidation-spoiled white wines. *J. Agric. Food Chem.* **2003**, *51*, 1377–1381.

(15) Cullere, L.; Cacho, J.; Ferreira, V. An assessment of the role played by some oxidation related aldehydes in wine aroma. *J. Agric. Food Chem.* **2007**, *55*, 876–881.

(16) Rodrigues, A.; Ferreira, A. C. S.; Guedes de Pinho, P.; Bento, F.; Geraldo, D. Resistance to oxidation of white wines assessed by voltammetric means. *J. Agric. Food Chem.* **2007**, *55*, 10557–10562.

(17) Lopes, P.; Silva, M. A.; Pons, A.; Tominaga, T.; Lavigne, V.; Saucier, C.; Darriet, P.; Teissedre, P. L.; Dubourdieu, D. Impact of oxygen dissolved at bottling and transmitted through closures on the composition and sensory properties of a Sauvignon Blanc wine during bottle storage. *J. Agric. Food Chem.* **2009**, *57*, 10261–10270.

(18) Heras, M. O.; Rivero-Perez, M. D.; Perez-Magarino, S.; Gonzalez-Huerta, C.; Gonzalez-Sanjose, M. L. Changes in the volatile composition of red wines during aging in oak barrels due to microoxygenation treatment applied before malolactic fermentation. *Eur. Food Res. Technol.* **2008**, *226*, 1485–1493.

(19) Karbowiak, T.; Gougeon, R. D.; Alinc, J. B.; Brachais, L.; Debeaufort, F.; Voilley, A.; Chassagne, D. Wine oxidation and the role of cork. *Crit. Rev. Food Sci. Nutr.* **2010**, *50*, 20–52.

(20) Li, H.; Guo, A.; Wang, H. Mechanisms of oxidative browning of wine. *Food Chem.* **2008**, *108*, 1–13.

(21) Bosso, A.; Guaita, M.; Vaudano, E.; Di Stefano, R. Influenza dell'ossigeno sull'evoluzione dei composti fenolici durante la conservazione dei vini rossi. Implicazioni sensoriali. *Ind. Bevande* **2000**, *29*, 630–640.

(22) Moutounet, M.; Mazauric, J. P.; Ducournau, P.; Lemaire, T. Micro-oxygénation des vins. Principe et applications technologiques. *Ind. Bevande* **2001**, *30*, 253–258.

(23) Perez-Magarino, S.; Sanchez-Iglesias, M.; Ortega-Heras, M.; Gonzalez-Huerta, C.; Gonzalez-Sanjose, M. L. Colour stabilization of red wines by microoxygenation treatment before malolactic fermentation. *Food Chem.* **2007**, *101*, 881–893.

(24) Amati, A.; Arfelli, G.; Castellari, M.; Simoni, M. Effetto dell'ossigenazione controllata sulla frazione fenolica dei vini rossi. *Ind. Bevande* **2000**, *29*, 606–612.

(25) Castel, C.; Morand, A.; Pujol, G.; Naudin, R. Influence de la micro-oxygénation sur la composition phenolique et les caracters sensoriels des vins rouges. *Ind. Bevande* **2001**, *30*, 271–276.

(26) Ferrarini, R.; Girardi, F.; De-Conti, D.; Castellari, M. Esperienze di applicazione della micro-ossigenazione come tecnica d'affinamento dei vini. *Ind. Bevande* **2001**, *30*, 116–122.

(27) Bertuccioli, M.; Rosi, I.; Lencioni, L.; Zini, S.; Siliani, A. Influenza dell'ossigeno sul profilo sensoriale del vino. L'esempio del vino da uve Sangiovese. *Ind. Bevande* **2001**, *30*, 489–495.

(28) Gerbi, V.; Caudana., A.; Zeppa, G.; Cagnasso, E. Esperienze di micro- ossigenazione su vini rossi piemontesi. *Ind. Bevande* **2001**, *30*, 496–500.

(29) Carrillo, J. D.; Salazar, C.; Moreta, C.; Tena, M. T. Determination of phthalates in wine by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry: Fibre comparison and selection. *J. Chromatogr., A* **2007**, *1164*, 248–261.

(30) Tena, M. T.; Carrillo, J. D. Multiple solid-phase microextraction: Theory and applications. *TrAC, Trends Anal. Chem.* **2007**, *26*, 206–214.

(31) Setkova, L.; Risticevic, S.; Pawliszyn, J. Rapid headspace solid-phase microextraction-gas chromatographic-time-of-flight mass spectrometric method for qualitative profiling of ice wine volatile fraction - I. Method development and optimization. *J. Chromatogr., A* **2007**, *1147*, 213–223.

(32) Trygg, J.; Wold, S. Orthogonal projections to latent structures (O-PLS). *J. Chemom.* **2002**, *16*, 119–128.

(33) Holmes, E.; Loo, R. L.; Stamler, J.; Bictash, M.; Yap, I. K. S.; Chan, Q.; Ebbels, T.; De Iorio, M.; Brown, I. J.; Veselkov, K. A.; Daviglus, M. L.; Kesteloot, H.; Ueshima, H.; Zhao, L. C.; Nicholson, J. K.; Elliott, P. Human metabolic phenotype diversity and its association with diet and blood pressure. *Nature* **2008**, *453*, 396–400.

(34) Ferreira, V.; San Juan, F.; Escudero, A.; Cullere, L.; Fernandez-Zurbano, P.; Saenz-Navajas, M. P.; Cacho, J. Modeling quality of premium Spanish red wines from gas chromatography-olfactometry data. *J. Agric. Food Chem.* **2009**, *57*, 7490–7498.

(35) Ferreira, V.; Fernandez, P.; Pena, C.; Escudero, A.; Cacho, J. F. Investigation on the role played by fermentation esters in the aroma of young spanish wines by multivariate-analysis. *J. Sci. Food Agric.* **1995**, *67*, 381–392.

(36) Perez-Prieto, L. J.; Lopez-Roca, J. M.; Gomez-Plaza, E. Differences in major volatile compounds of red wines according to storage length and storage conditions. *J. Food Compos. Anal.* **2003**, *16*, 697–705.

(37) Escalona, H.; Birkmyre, L.; Piggott, J. R.; Paterson, A. Effect of maturation in small oak casks on the volatility of red wine aroma compounds. *Anal. Chim. Acta* **2002**, *458*, 45–54.

(38) Gurbuz, O.; Rouseff, J. M.; Rouseff, R. L. Comparison of aroma volatiles in commercial Merlot and Cabernet Sauvignon wines using gas chromatography - Olfactometry and gas chromatography - Mass spectrometry. *J. Agric. Food Chem.* **2006**, *54*, 3990–3996.

(39) Camara, J. S.; Alves, M. A.; Marques, J. C. Changes in volatile composition of Madeira wines during their oxidative ageing. *Anal. Chim. Acta* **2006**, *563*, 188–197.

(40) Hernandez-Orte, P.; Lapena, A. C.; Escudero, A.; Astrain, J.; Baron, C.; Pardo, I.; Polo, L.; Ferrer, S.; Cacho, J.; Ferreira, V. Effect of micro-oxygenation on the evolution of aromatic compounds in wines: Malolactic fermentation and ageing in wood. *LWT—Food Sci. Technol.* **2009**, *42*, 391–401.

(41) Cullere, L.; Escudero, A.; Cacho, J.; Ferreira, V. Gas chromatography-olfactometry and chemical quantitative study of the aroma of six premium quality Spanish aged red wines. *J. Agric. Food Chem.* **2004**, *52*, 1653–1660.

(42) Rapp, A.; Mandery, H. Wine aroma. *Experientia* **1986**, *42*, 873–884.

(43) Schreier, P. Flavor composition of wines: A review. *Crit. Rev. Food Sci. Nutr.* **1979**, *12*, 59–111.

(44) Es-Safi, N. E.; Cheynier, V.; Moutounet, M. Study of the reactions between (+)-catechin and furfural derivatives in the presence or absence of anthocyanins and their implication in food color change. *J. Agric. Food Chem.* **2000**, *48*, 5946–5954.

(45) Es-Safi, N. E.; Cheynier, V.; Moutounet, M. Role of aldehydic derivatives in the condensation of phenolic compounds with emphasis on the sensorial properties of fruit-derived foods. *J. Agric. Food Chem.* **2002**, *50*, 5571–5585.

(46) Es-Safi, N. E.; Cheynier, V.; Moutounet, M. Implication of phenolic reactions in food organoleptic properties. *J. Food Compos. Anal.* **2003**, *16*, 535–553.

(47) Aznar, M.; Lopez, R.; Cacho, J.; Ferreira, V. Prediction of aged red wine aroma properties from aroma chemical composition. Partial least squares regression models. *J. Agric. Food Chem.* **2003**, *51*, 2700–2707.

(48) Caille, S.; Samson, A.; Wirth, J.; Dieval, J. B.; Vidal, S.; Cheynier, V. Sensory characteristics changes of red Grenache wines submitted to different oxygen exposures pre and post bottling. *Anal. Chim. Acta* **2010**, *660*, 35–42.

(49) Cano-Lopez, M.; Pardo-Minguez, F.; Schmauch, G.; Saucier, C.; Teissedre, P. L.; Lopez-Roca, J. M.; Gomez-Plaza, E. Effect of micro-oxygenation on color and anthocyanin-related compounds of wines with different phenolic contents. *J. Agric. Food Chem.* **2008**, *56*, 5932–5941.

(50) de Beer, D.; Joubert, E.; Marais, J; Manley, M. Effect of oxygenation during maturation on phenolic composition, total antioxidant capacity, color and sensory quality of pinotage wine. *S. Afr. J. Enol. Vitic.* **2008**, *29*, 13–25.

(51) Etaio, I.; Elortondo, F. J. P.; Albisu, M.; Gaston, E.; Schlich, P. Sensory attribute evolution in bottled young red wines from Rioja Alavesa. *Eur. Food Res. Technol.* **2009**, *228*, 695–705.

(52) Schmarr, H. G.; Bernhardt, J.; Fischer, U.; Stephan, A.; Muller, P.; Durner, D. Two-dimensional gas chromatographic profiling as a tool for a rapid screening of the changes in volatile composition occurring due to microoxygenation of red wines. *Anal. Chim. Acta* **2010**, *672*, 114–123.