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The Combined Effects of Storage Temperature and Packaging on the Sensory, Chemical, and Physical Properties of a Cabernet Sauvignon Wine

Helene Hopfer,* Peter A. Buffon, Susan E. Ebeler, and Hildegarde Heymann

Department of Viticulture & Enology, University of California, Davis, One Shields Avenue, Davis, California 95616, United States

Supporting Information

ABSTRACT: A Californian Cabernet Sauvignon was stored for 6 months at three different constant temperatures to study the combined effects of storage temperature and packaging configuration. Glass bottles with natural cork, synthetic cork, and screw cap closure, as well as two Bag-in-Box treatments, were used in the experiment. A trained sensory panel was able to detect significant changes in aroma, flavor, taste, mouthfeel, and color attributes among the samples, differences that were found also with various chemical and physical measurements (volatile profile, polyphenol pattern, enological parameters, color space). Additionally, two commonly used polyphenol assays were compared to each other in terms of their ability to detect the changes in the polyphenol profile. Generally, sample changes were more pronounced due to the different storage temperatures, with 30 sensory attributes differing significantly among the three different storage temperatures, while only 17 sensory attributes showed a significant packaging effect. With increasing storage temperature the packaging effect became more pronounced, resulting in the largest changes in the Bag-in-Box samples stored at the highest temperature of 40 °C. At the highest storage temperature, all wines showed oxidized characters, independent of the wine packaging configurations, but to a varying degree. Generally, wines that received highest oxygen amounts and storage temperatures were much lighter, less red, and more brown-yellow at the end of the 6-month storage period, compared to their counterparts stored at 10 °C. These changes in color and polyphenols, respectively, were also detected with the two spectrophotometric assays. With increasing storage temperature both assays measured reduced concentrations in total phenols and total anthocyanins, while total tannins, degree of ionized anthocyanins, and color density increased. Various volatile compounds differed significantly among the samples, with largest relative concentration changes in acetates, organic acids, and alcohols, in good agreement with previous literature reports, with some being well correlated to specific sensory attributes too; for example, various acetates correlated to cherry and fruit aromas and flavors. The study shows that storage at elevated temperatures could be a valuable tool for wine packaging screening and testing new and improved wine packaging types under the worst conditions, which are unfortunately not unrealistic.

KEYWORDS: *wine packaging, storage temperature, oxidation, sensory analysis, wine color*

INTRODUCTION

The conservation of wine during storage is in most cases outside of the control of the winemakers; yet, improper storage is often the reason for consumer complaints due to the formation of oxidative characters. The formation of oxidative characters can be tied back to improper oxygen management during winemaking and/or bottling and/or improper shipping or storage (i.e., high-temperature exposure) due to accelerated aging and early oxidation of wine.[1−5] Despite the high prices and perceived value of aged red wines, most wines sold are produced for consumption within a year after release. Further, most wines are typically consumed within three days after purchase[6] with the exception of age-worthy wines specifically made for a longer storage period.

One might argue that high-temperature storage is not an intended way to store wines, but unfortunately this is experienced more often than desired, as shown by Butzke et al.[5] Shipping model wines across the United States during summer and fall of 2009, the authors observed diurnal temperature changes in the air around the wine bottle between −13 and 44 °C for wines that were shipped without thermal blankets. The use of thermal blankets protected the wines to some extent against elevated temperatures and temperature spikes during shipping. Additionally, a temperature difference of 2−4 °C was observed between the air around the wine bottle and the liquid inside the bottle, indicating a certain degree of some heat protection by the glass. The authors did not conduct any sensory analysis on the heat-damaged wines, but another research group[7] simulated shipping under four less severe temperatures (20 °C, 40 °C, cycling between 20 and 40 °C, and 10 °C with movement over a period of 3 weeks) and studied the chemical and sensory changes in the shipped white and red wines. Robinson et al.[7] found 30 volatiles in Cabernet Sauvignon wines that differed significantly among the different storage conditions, while the trained sensory panel detected significant changes in dried fruit and canned vegetable characteristics.

Oxidation in wines is highly dependent on various factors such as storage conditions, packaging type, presence of antioxidants, amount of oxygen in the packaging, and much more. Due to

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their winemaking process (e.g., less skin contact time with subsequent less extraction of phenolics and no or only short time barrel aging), white wines are typically more prone to oxidation than red wines, and several studies looked at the impact of various parameters on white wine conservation, including storage temperature, packaging type, and winemaking procedures.[4,8−11]

However, oxidation reactions take place in any wine, and these reactions are even sped up when wine is stored at higher temperatures. Various aspects of wine oxidation are studied such as changes in polyphenols,[12−15] the effects of different oxygen levels,[16−20] or storage conditions, including wine packaging and storage temperature.[2,3,7,9,16,21] These changes were studied in different *Vitis vinifera* varieties, including Cabernet Sauvignon wines,[3,7,16−18,21,22] but also Syrah,[19] Grenache,[23−25] Cabernet Franc, [21] and other monovarietal and blended red wines from Spain and Italy.[13,18]

Additionally, several volatile compounds have been reported as oxidation products or oxidation-related compounds in Cabernet Sauvignon.[26,27] Lee et al.[16] identified eight volatiles that correlated either positively or negatively to the degree of oxidation in Cabernet Sauvignon in a short-term shelf-life study, including isoamyl acetate, ethyl decanoate, nonanoic acid, decanoic acid, 2-furancarboxylic acid, dodecanoic acid, and phenylacetaldehyde.

Robinson et al.[7] found decreased levels of linalool and various ethyl esters for Cabernet Sauvignon wines stored at 40 °C, while ethyl-2-furoate, ethyl phenylacetaldehyde, *p*-cymene, 1,1,6-trimethyl-1,2-dihydronaphthalene, and both vitispirane 1 and 2 increased in concentration when compared to a lower storage temperature of 20 °C. Similarly, these volatiles were reported in other varieties too, such as Tempranillo, Merlot, Cabernet Franc, Grenache, and others.[7,18]

In a recent study by Balboa-Lagunero and co-workers[18] on 65 Spanish red and white wines that underwent natural and "forced" oxidation, the sensory changes with an increase in oxidation descriptors (cognac/brandy/sherry wine, old wine/matured wine) and the decrease or loss of herbal, fresh, fruity, and flowery notes were linked to increased concentrations in methional, (*Z*)-2-nonenal, (*E*)-2-octenal, furaneol, dodecanal, (*Z*)-whiskey lactone, and *o*-aminoacetophenone and decreased concentrations in volatiles such as (*Z*)-3-hexenol, ethyl hexanoate, and isoeugenol. Similarly to Bueno et al.,[28] the authors found that especially aldehydes are formed in high amounts, in the range 100−200 μg/L, during oxidation.

Besides storage temperature, the packaging configuration for wine was shown to impact shelf life as well. In a two-year closure study including screw caps and natural and synthetic corks, Kwiatkowski and co-workers[3] observed that wines aged differently depending on the closure used at bottling. Significant differences in SO_2 levels, polyphenol measurements, and color space values and reduced and oxidized sensory characters were found among the different closures, with the highest scores of reduced character in the extreme case of screw caps with very small headspace volumes. The authors reported that the wines did not simply age at different rates with the different closures but rather developed different chemical and sensory profiles, which became more pronounced later in the storage experiment.

The impact of postbottling oxygen ingress on the formation of volatile sulfur compounds such as H_2S, methyl mercaptan, and other thiols and sulfides, which are all known contributors to the so-called reduced characters in wines, was evaluated by Ugliano et al.[19] in two Syrah wines. In combination with micro-oxygenation prior to bottling and three different oxygen levels during filling, the authors found that low postbottling oxygen led to significantly higher concentrations in H_2S and methyl mercaptan, but showed no significant effect on the studied sulfides dimethyl disulfide, *S*-methyl thioacetate, and dimethyl sulfide, with the latter one being formed during bottle aging independent of the oxygen concentration.

In a more specific study, Blake et al.[21] demonstrated the effect of wine packaging on the methoxy pyrazine concentrations in Riesling and Cabernet Franc wines and found that over a period of 18 months wines packaged in Tetrapak or synthetic corks lost higher amounts of the methoxy pyrazines than natural cork or screw cap closures. The authors speculate that the observed changes among the different packaging types resulted from both differences in gas permability and sorption phenomena. Wines stored in Tetrapak were also the highest in red pigments and A420 nm and A520 nm values, most likely due to the higher oxygen ingress over time.

The effect of wine packaging on wine conservation was studied by Ghidossi et al.[29] by comparing the changes of red Bordeaux wine stored in either glass bottles, polyethylene terephthalate (PET) bottles, or 3 L Bag-in-box (BIB) containers over a storage period of 18 months at 20 °C. Oxygen was consumed within the first 3 months of storage in all packaging configurations, and an increase in dissolved oxygen was observed for the BIB samples after 6 months, indicating oxygen ingress through the packaging. Similarly, CO_2 and SO_2 levels decreased in all packaging configurations, while color was not affected for any of the packaging types after 18 months. Sensorially, the panel perceived significant differences in fruity character, oxidative evolution, astringency, and bitterness for the BIB and PET packaging compared to the glass bottles.

Red Apulian table wines were studied by Mentana et al.,[30] where the authors looked at chemical changes due to different packaging (glass bottles and PET bottles with and without oxygen scavenger). Significant changes in enological parameters, anthocyanin fraction, volatiles, and sensory properties were detected due to the different packages, with the largest changes in the normal PET bottles compared to the glass bottles. Flavor scalping (i.e., reduced amounts of various alcohols and ethyl esters) was observed to a higher extent in the normal PET bottle when compared to the PET bottle with oxygen scavengers. PET bottles with oxygen scavengers were more similar to the glass bottles, with no significant sensory differences between the two packaging types.

In red wines, wine phenolics are an important class of compounds, responsible for the perception of astringency, bitterness, and the color of red wine. In addition, they react with oxygen, contributing to the changes in wine due to aging and/or oxidation.[31] It was shown that increasing storage time decreases the concentrations of proanthocyanidinis and hydroxycinnamic acid, independent of the amount of oxygen present, while anthocyanins and flavan-3-ol monomers decrease at a higher rate at higher oxygen concentrations.[25] The same authors propose that anthocyanins could be used as oxidation markers due to being the primary oxidation targets and speculate that the reaction of oxygen with anthocyanins partially protects other compounds from being oxidized. Generally, the decrease in anthocyanin levels over time is associated with a wine color change from purple to more red/orange.[12,15] Two commonly used assays for polyphenols are based on spectrophotometric measurements of red wine: the Harbertson−Adams assay[32−34] and the Somers assay.[35−37] Besides spectrophotometric measurements of wine polyphenols, the red wine color space is often expressed in CIELab units using a colorimeter. The CIELab

Table 1. Sample Description (sample codes together with packaging and temperature configuration) and Basic Chemical Measurements of Titratable Acidity (TA) in Tartaric Acid Equivalents (TAE), Volatile Acidity (VA) in Acetic Acid Equivalents (AAE), pH, Ethanol Content, Free and Total SO_2[a]

		code	TA [g/L]	VA [g/L]	pH	EtOH [v %]	free SO_2 [mg/L][c]	total SO_2 [mg/L][c]
before bottling			6.3	0.59	3.58	13.1	54	131
bottle with natural cork[b]	10 °C	*naco10*	6.2 fg	0.47 c	3.71 a	13.07 a	31 a	106 abc
	20 °C	*naco20*	6.1 g	0.48 bc	3.71 a	13.06 a	24 abc	106 abc
	40 °C	*naco40*	6.0 h	0.61 a	3.72 a	13.03 a	n.d. d	74 cd
bottle with synthetic cork[b]	10 °C	*syco10*	6.3 abcd	0.65 a	3.72 a	13.09 a	30 a	129 a
	20 °C	*syco20*	6.2 cde	0.63 a	3.72 a	13.08 a	24 abc	111 ab
	40 °C	*syco40*	6.2 g	0.60 a	3.73 a	13.05 a	n.d. d	82 bcd
bottle with screw cap[b]	10 °C	*screw10*	6.2 cde	0.65 a	3.70 a	13.08 a	28 ab	109 ab
	20 °C	*screw20*	6.2 ef	0.65 a	3.70 a	13.04 a	29 ab	104 abc
	40 °C	*screw40*	6.1 g	0.64 a	3.70 a	13.06 a	n.d. d	69 d
BIB filled at normal O_2 atm[b]	10 °C	*bib10*	6.2 de	0.62 a	3.74 a	13.08 a	28 abc	100 abcd
	20 °C	*bib20*	6.2 e	0.59 abc	3.74 a	13.13 a	21 bc	105 abc
	40 °C	*bib40*	6.3 bcde	0.57 abc	3.73 a	12.16 b	n.d. d	n.d. e
BIB filled at reduced O_2 atm[b]	10 °C	*map10*	6.3 a	0.59 ab	3.70 a	13.09 a	20 c	104 abc
	20 °C	*map20*	6.3 abc	0.65 a	3.73 a	13.13 a	26 abc	98 abcd
	40 °C	*map40*	6.3 ab	0.57 abc	3.70 a	12.31 b	n.d.	n.d.
HSD			0.06	0.123		0.313	8.3	32.5

[a]Reported values are mean values for three replicate determinations, shown together with Tukey's honestly significant differences (HSD), determined after the 6-month storage period as described in the Materials and Methods section. Columns that share the same lowercase letter are not significantly different from each other ($p \leq 0.05$). Values determined at the donating winery prior to the bottling and filling of the samples are added for ease of comparison, but different methods were used to determine the ethanol content. [b]BIB, 3 L DuraShield 34ES Bag-in-Box (Scholle Packaging, Nohlake, IL); bottles, 0.75 L green glass bottles; corks, 24 mm × 49 mm AC-1 grade natural cork (ACI Cork, Fairfield, CA) or 22.5 mm × 43 mm Classic+ synthetic cork (Nomacorc LLC); and screw cap, aluminum Stelvin cap 30 mm × 60 mm (Federfin Tech S.R.L., Tromello, Italy) with 28.6 mm × 2 mm tin-PVDC liner (Oenoseal, Chazay D'Azergues, France). [c]Limits of quantitation (LOQ), 10 mg/L.

values span a three-dimensional color space, defining each color by their L^*, a^*, and b^* values. The CIELab color space was shown to correlate well to human color perception,[38] as well as monomeric anthocyanins and total anthocyanins.[39,40]

All these studies separately showed the effect of storage conditions or packaging type on wine conservation. However, no study so far looked at the combined effects of both factors. Thus, in the presented work we studied the combined effects of storage temperature and packaging type on the sensory, chemical, and physical characteristics of red Cabernet Sauvignon wine. Sensory descriptive analysis (DA) is a method that employs trained human subjects to quantitatively and qualitatively reveal product attributes. In this study we used a trained sensory panel to detect changes in aroma, flavor, taste, mouthfeel, and color attributes. All these sensory attributes were correlated in a partial least squares regression (PLS) to instrumental-chemical measurements of volatiles, polyphenols, and wine color, to study which chemical or physical measurement best predicts the sensory response.

MATERIALS AND METHODS

Experimental Design. A total of 15 treatments were realized in the study as a result of three different storage temperatures (10, 20, 40 °C) and five different wine packaging types (glass bottle with natural corks, synthetic corks, and screw caps and Bag-in-Box filled under normal and reduced oxygen concentrations; Table 1). After filling and bottling, samples were assigned to their respective storage temperature treatments and stored for 6 months in the dark, similarly as described earlier.[10]

Samples and Materials. A commercial grade Cabernet Sauvignon (vintage 2009) from the Californian Central Coast American Viticultural Area (AVA) was used for all samples. The wine neither was treated with ascorbic acid nor contained CO_2. The donating winery analyzed the ethanol content (13.1% v/v), specific gravity (0.998 g/cm^3), titratable acidity (6.3 g/L), volatile acidity (0.59 g/L), reducing sugar (7.9 g/L), total and free SO_2 concentration (131 and 54 mg/L), pH (3.58), and dissolved oxygen (0.51 mg/L) immediately before the filling and bottling of the samples took place. These measurements were repeated after the storage period using the methods as described in the Materials and Methods section (Table 1).

All volatile compounds except those described below were purchased from Sigma-Aldrich (St. Louis, MO, USA; purity >80%). (+)-Catechin, malvidin 3-glucoside, sodium metabisulfite, acetaldehyde (natural 50% solution in ethanol), triethanolamine, ferric chloride hexahydrate, albumin from bovine serum, maleic acid, glacial acetic acid, and sodium chloride were also purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethyl-2-methylbutyrate (SAFISIS, Soustons, France), linalool (Alfa Aesar, Ward Hill, MA, USA), acetic acid (EMD, Merck, Darmstadt, Germany), 2-methylbutanoic acid (TCI America, Portland, OR, USA), hexanoic acid (Thermo Fisher Scientific, Geel, Belgium), and propionic acid (MP Biomedicals, Solon, OH, USA), all with a purity of >80%, were purchased from their respective producers. Ultrapure water (Milli-Q, Billerica, MA, USA, 18 MΩ), 200 proof ethanol (Goldshield, Hayward, CA, USA), urea (ultrapure, USB, Cleveland, OH, USA), potassium metabisulfite (Mallinckrodt, St. Louis, MO, USA), potassium bitartrate, sodium hydroxide, and hydrochloric acid (all from Fisher Scientific, Pittsburgh, PA, USA) were used in the analyses.

Bottling and Filling of Samples. All the samples were filled and bottled within two days in April 2011. On the first day we filled the Bag-in-Box samples in an industrial facility in Madera, CA. The filling line uses modified atmosphere packaging (MAP) conditions to fill the BIB at lower oxygen concentrations (down to 1−2% oxygen). We realized two different BIB treatments by filling samples with and without the MAP system switched on, to study the impact of the reduced oxygen content during filling on the wine properties after the 6-month storage period. The MAP samples were filled first, then the MAP system was switched off, and after an hour of equilibration, the samples were filled under normal oxygen concentrations (21% oxygen). For each of the two BIB treatments, three BIB bags were equipped with oxygen sensors and inserted in the filling process spread over the whole filling period. A total of 6 × 8 (2 filling conditions (MAP and non-MAP) × 3 storage temperatures × 8 BIB with 3 L each) BIBs were filled. After filling, all BIB samples as well as a 227 L stainless steel drum, chilled to

Table 2. Reference Standards Used in the Descriptive Analysis (DA)[a]

Aromas and Flavors		
red fruit		1 tsp black cherry juice concentrate (RW Knudsen, Chico, CA)
		+ 1 frozen strawberry (Dole, West Village, CA)
		+ 5 g cut Roma tomatoes (0.5 × 0.5 cm pieces)
		+ 10 halved fresh raspberries (Driscoll's, Watsonville, CA)
		+ 6 halved dried cranberries (Mariani Premium, Vacaville, CA)
		+ 2 dried bing cherries cut in 6 pieces (Trader Joe's, Monrovia, CA) in 20 mL base wine
cherry		5 mL black cherry juice concentrate (RW Knudsen, Chico, CA)
jammy		15 g Mary Ellen blackberry jam (J.M. Smucker Co., Orrville, OH)
		+ 15 g fresh raspberries jam (Trader Joe's, Monrovia, CA)
		+ 10 g Mary Ellen red plum jam (J.M. Smucker Co., Orrville, OH) in 20 mL base wine
grapefruit		2 cm × 1 cm fresh grapefruit peel
fresh veggie		5 g fresh green bell pepper cut into 5 × 5 mm pieces
		+ 5 g fresh green beans cut into 5 × 5 mm pieces
		+ 1 g fresh white leek cut into 5 × 5 mm pieces in 20 mL base wine
canned veggie		5 mL brine cut asparagus with tips (Sunny Select, Walnut Creek, CA)
		+ 5 mL brine Libby's whole kernel sweet corn (Seneca Foods Co., Marion, NY)
		+ 5 mL brine Green Giant cut green beans (Minneapolis, MN) in 20 mL base wine
earthy		2 g all-purpose potting soil (Black Gold, Bellevue, WA)
		+ 10 drops water
wood[b]	woody	0.1 g EvOak American oak powder (Oak Solutions, Napa, CA)
		+ 0.1 g EvOak French oak medium toast large chips (Oak Solutions, Napa, CA) in 25 mL base wine
	cedar	1 cedar ball (CedarFresh, Household Essentails, Hazelwood, MO)
black pepper		0.13 g ground black pepper corns (Safeway, Pleasanton, CA) in 20 mL base wine
spice		0.5 g star anise (Davis Food Coop, Davis, CA)
		+ 0.05 g ground cinnamon (Davis Food Coop, Davis, CA)
		+ 0.01 g ground cloves (Davis Food Coop, Davis, CA) in 25 mL base wine
molasses/ soy sauce		5 mL soy sauce (Kikkoman, San Francisco, CA)
		+ 1.5 g molasses from blue agave in 40 mL base wine
brown flavor		1 tsp brown cane sugar
		+ 0.1 mL vanilla extract (Kirkland, Costco)
dried fruit		5 raisins (SunMaid, Stockton, CA)
		+ 1/2 dried prune (SunMaid, Stockton, CA)
		+ 1/2 dried apicot (SunMaid, Stockton, CA) in 25 mL base wine
oxidized[b]	honey	3.5 g honey (Nugget, Woodland, CA) in 25 mL base wine
	sherry	10 mL Domecq Light Sherry Manzanilla
	port wine	10 mL Prager Petit Sirah Port Lodi
chemical[b]	solvent	2 mL 95% EtOH (GoldShield, Hayward, CA)
		+ 200 μL ethyl acetate (Fisher Scientific, Pittsburgh, PA)
		+ 200 μL distilled white vinegar (Best Yet, Bethpage, NY) in 25 mL base wine
	SO_2/ biting	10 dried sulfured bing cherries (Trader Joe's, Monrovia, CA) in 20 mL base wine
floral		0.5 g Nivea Crème (Beiersdrof, Wilton, CT)
		+ 0.1 mL violet essential oil (Aroma Crafts, Uttaranchal, India) solution (2 drops in 10 mL water)
Tastes and Mouthfeel		
sour		2 g/L L-(+)-tartaric acid (Fisher Scientific, Pittsburgh, PA) in water
sweet		7 g/L sucrose (pure cane sugar, C&H, Crockett, CA) in water
bitter		1 g/L caffeine (Sigma Aldrich, St. Louis, MO) in water
astringent		0.43 g/L alumn (McCormick, Sparks, MD) in water
hot		8% (v/v) ethanol (Vodka 80 proof) in water
viscous		1.5 g/L carboxymethylcellulose sodium salt (Sigma Aldrich, St. Louis, MO) in water
Color		
ACE paint		F2, F5, B6, B7, B8
Benjamin Moore		009, 2005, 2074, 2078, 2079, 2080, 2081, 2083, 2084, 2085, 2087, 2091, 2092, 2093, 2173, 2174

[a]As base wine Franzia Caberent Sauvignon (Ripon, CA) was used unless otherwise noted. All attributes were anchored with the words "low" and "high", with the exception of viscous ("thin" and "thick"). [b]For this reference, more than one standard was available, but panelists rated only the combined attribute.

4 °C and filled with the same wine as the BIB samples, were transported to UC Davis and stored at 4 °C. While all BIB samples were kept at 4 °C for 4 days before they were transferred in their respective storage temperature units, the stainless steel keg was used the next day for filling all bottle treatments. Prior to bottling, the wine was Steri-filtered with a 0.45 μm membrane filter (Pall, Port Washington, NY, USA) and bottled on a six-position bottling line (Costral Fiamat 2000, Riquewihr, France). The wine was moved with high-purity nitrogen, and the headspace of all bottles and the filler bowl was sparged with nitrogen to avoid oxygen pick-up. Oxygen levels were constantly checked in the bottle throughout the filling process by inserting the oxygen sensor equipped bottles throughout the filling process. For each of the nine bottle treatments (3 closure types × 3 storage temperatures) a case of wine was filled. Filled bottles were kept upright and at 4 °C for 3 days before they were transferred into their respective storage units.

Storage Conditions. Samples were stored at 10 °C in a temperature-controlled chill room with a mean temperature of 10.0 ± 1.0 °C during the whole period. All samples were placed close together in one corner of the room. For the 20 °C storage, samples were stored in a temperature-controlled room used for sensory evaluation, locked away in cabinets. The average temperature was 20.8 ± 1.3 °C, monitored with four temperature loggers (Tinytag Transit 2 TG4080, Gemini Data Loggers, West Sussex, U.K.). Samples were held at 43.5 ± 1.0 °C in four 200 L temperature-controlled tanks (designed, fabricated, and donated by a team of research engineers led by T. J. Rogers, Cypress Semiconductors, San Jose, CA, USA), equipped with temperature sensors (HOBO U12 four-channel external data logger with four TMC-HD temperature probes).

Oxygen Measurements. During the storage period, both headspace and dissolved oxygen levels were checked a total of 21 times, using noninvasive oxygen sensors (5 mm sensor spots PSt3, NomaSense, Nomacorc LLC, Zebulon, NC, USA). Two bottles and one BIB of each treatment were equipped with the oxygen sensors. Each bottle was equipped with one sensor positioned in the neck of the bottle above the headspace (HS) to measure the HS oxygen, and the second sensor positioned at mid height of the bottle for measurement of the dissolved oxygen (DO). In the BIB, the sensor dot was glued on the inside near the spout, and both HS and DO measurements were taken

using the same sensor by initially reading the HS value and then inverting the BIB, waiting 5−10 min, and reading the DO value. Within the first 2 weeks oxygen levels were checked five times per week, followed by three readings per week for the subsequent week, and once a week thereafter. Oxygen readings were automatically temperature-corrected using the attached temperature probe and after an equilibrium was reached. HS values were measured in hPa and % oxygen, while DO was measured in ppm, with limits of detection (LODs) of 0.31 hPa and 15 ppb/0.015 ppm, respectively, according to the manufacturer's specifications. Total packaging oxygen (TPO) in ppm was calculated as the sum of DO and HS values after converting HS values into ppm, assuming a constant HS volume in the bottles of 4.71 mL, and measuring the HS volume in the BIB with the BIB cone meter.[41] Similarly to our previous study, we used the area under the total packaging oxygen curve (*auc*) in ppm per day (ppm/day) for each treatment after averaging over bottle replicates for further analyses and correlations. We could show in our previous study[10] that the *auc* values correlate well with the state of the samples in a sense that samples with low oxygen consumption and/or ingress (e.g., stored at lower temperatures in screw capped bottles) have a higher *auc* than samples stored at higher temperatures. The *auc* is therefore a single value expressing oxygen consumption.

Sensory Analysis. A generic descriptive analysis adapted from ref 42 was performed to describe differences in the samples using aroma, flavor, taste, mouthfeel, and color attributes listed in Table 2. Ten panelists (nine females), some with previous experience in wine and/or food descriptive analysis, were recruited based on their availability and commitment to participate, from the students, staff, and retirees of the Departments of Food Science & Technology and Viticulture & Enology at UC Davis. The panelists were on average 33.8 years old (±10.3 yrs). A recent study by Heymann et al. [43] showed that 8 trained panelists are capable of providing the same significant results in a red wine DA as 18 trained panelists, and therefore the number of 10 trained panelists is an adequate number. The Institutional Review Board (IRB) at UC Davis approved the study (protocol no. 201018548-1), and all panelists gave informed oral consent and received no financial compensation for their participation. Snacks were served after each training and evaluation session.

During five one-hour-long training sessions over a period of 2 weeks the panelists created, agreed on, and were trained in the listed attributes (Table 2). During the training period all samples were presented to the panelists at least once without them knowing how many different samples they were evaluating. None of the panelists were aware of the purpose of the study nor how many replicate sessions or different samples they were evaluating.

Following training, wine samples were evaluated over a period of 3 weeks; all samples were tested in triplicate with six wines served per session in an incomplete random block design using a modified William Latin square (WLS), provided by FIZZ (Biosystemes, Couternon, France). The FIZZ software was also used for collecting the attribute scores on an end point labeled and anchored line scale. A WLS design controls for carryover effects between samples. For the aroma, flavor, taste, and mouthfeel attributes, sample volumes of 25 mL were tasted in black pear-shaped ISO glasses,[44] labeled with three-digit random codes, in individual tasting booths equipped with positive air flow and white light. All samples had to be expectorated, and filtered water (Arrowhead, Nestle Waters America, Stamford, CT, USA) and unsalted crackers (Nabisco unsalted top premium saltine crackers, Kraft Foods, Northfield, IL, USA) were provided for palate cleansing. A one-minute break between each wine and a three-minute break between the third and fourth wine were included to decrease palate fatigue.

The color evaluations were carried out in a separate booth with sample volumes of 25 mL in clear pear-shaped ISO glasses together with the reference paint chips from a local hardware store (ACE Hardware, Davis, CA, USA) and an evaluation sheet. All color evaluations took place in individual booths under defined illumination conditions as described in detail in ref 10. The CIELab color space values (L^*, a^*, b^*) of all used reference color chips were measured with a chromameter (Konica Minolta Sensing Americas, Inc., Ramsey, NJ, USA) in triplicate and used for all further analyses.

Chemical and Physical Analyses. As described in ref 10, the CIELab color space was measured with a chromameter in triplicate. Besides the directly measured L^*, a^*, and b^* values, the Chroma C^* and hue h values were calculated as described in ref 45. Besides this fast color measurement technique, we additionally included two different spectrophotometric assays that measure different aspects of wine phenolics, an important class of red wine compounds: the Harbertson−Adams assay[32−34] and the Somers assay.[35−37] Both methods are rapid, can be automated, and report total values, with some of them correlating to perceived astringency.[46] The Somers and Evans assay[35,37,47] consists of four treatments that evaluate the color stability before and after treating the wine with excess SO_2 to measure the SO_2-resistant pigments, excess acetaldehyde to estimate the colored anthocyanins at wine pH, and hydrochloric acid as an indicator for total red pigments and total phenolics[36] (chemical age 1 *CA1*, chemical age 2 *CA2*, degree of anthocyanin ionization *DIA*, total anthocyanin *tAS*, color density *CD*, SO_2-corrected color density *cCD*, hue *hS* (−), total phenolics *tP*, SO_2-resistant pigments *rPig*). The second assay, the Harbertson−Adams or protein precipitation assay, measures total iron-reactive phenolics (*IRP*) and total tannins (*tT*) as (+)-catechin equivalents, small and large polymeric pigments (*SPP*, *LPP*), and total anthocyanins (*tA*) as malvidin-3-glucoside equivalents.[32−34] All analyses were carried out on a BioMate 3S spectrophotometer (Thermo Fisher, Waltham, MA, USA) at wavelengths 510 and 520 nm in triplicate using polystyrene cuvettes (for the Harbertson−Adams assay) or at wavelengths 280, 420, and 520 nm in triplicate with methyl acrylate semicuvettes (for the Somers assay) both with a path length of 10 mm (VWR, Batavia, IL, USA, and BioRad, Hercules, CA, USA).

In addition, titratable (*TA*) and volatile acidity (*VA*), pH, ethanol (*EtOH*), and free and total SO_2 (*fSO2, tSO2*) were determined in triplicate as described in detail in ref 10. In short, TA expressed in tartaric acid equivalents (TAE), pH, and free and total SO_2 were measured as described by refs 48 and 49, while VA in acetic acid equivalents (AAE) was measured with an enzymatic kit (Unitech Scientific Flex-Reagent, Hawaiian Gardens, CA, USA). Ethanol levels were determined with an alcolyzer (Anton Paar, Graz, Austria).

For monitoring changes in the red wine volatile pattern we used a recently published method developed for the profiling of Cabernet Sauvignon wines using headspace−solid phase microextraction with gas chromatography−mass spectroscopy (HS-SPME-GC-MS),[50] with the additional measurement of diethyl succinate (Sigma-Aldrich, St. Louis, MO, USA). Internal-standard-normalized areas of selected ion monitoring ions were used for further analyses and to compare relative changes among the samples. All detected compounds together with their identification features are listed in Table 3.

Statistical Analyses. All statistical analyses used a significance level of 5%. Results from the sensory experiments were analyzed for the effects *judge J*, *packaging P*, *temperature T*, *replicate R*, and the *packaging*−*temperature* interaction *P:T* in an analysis of variance (ANOVA), if a prior multivariate analysis of variance (MANOVA) showed a significant *wine* effect, as described in detail in ref 10. Canonical variate analysis (CVA) on the aroma, flavor, taste, and mouthfeel attributes, as well as the sensory color results, was employed to create the sample space. Confidence intervals (CI) of 95% as described by Owen and Chmielewski[51] were created in R to present a visual significance testing of the sample differences in the CVA based on the sample variability.

The instrumental color measurements (chromameter and UV/vis spectrophotometer) and all chemical analyses were similarly analyzed using MANOVA and ANOVA, followed by correlation principal components analysis (PCA) to create the product spaces. Means followed by Tukey's HSD multiple comparisons were calculated for all analyses ($p \leq 0.05$).

As described in detail in ref 10, a repeated measure ANOVA was calculated on the oxygen data (headspace oxygen and dissolved oxygen changes over the storage period in all treatments), followed by the calculation of the areas under the curve for the oxygen consumption curves. Partial least squares analysis was employed to correlate and predict the sensory variables by the physical and chemical measurements.[52−54] Single value decomposition in a kernel algorithm was

employed as further explained by Mevik and Wehrens.[55] SAS (SAS Institute Inc., Cary, NC, USA) was used for the repeated measure ANOVA, and R with the SensoMineR(), candisc(), and pls() packages was used for all other analyses.[55−59]

RESULTS

Sensory Analysis. The MANOVA revealed significant differences among the wine samples ($p \leq 0.05$), using the aroma, flavor, taste, and mouthfeel attributes and the CIELab values from the color reference chips. From the subsequent ANOVA, most attributes differed significantly as a function of storage temperature (*T*) (12 aroma, 11 flavor, 1 taste, and 2 mouthfeel attributes, 4 color parameters). The packaging type (*P*) also significantly influenced a number of attributes (9 aroma, 10 flavor attributes, and 4 color parameters), while a significant packaging−temperature interaction (*P:T*) was observed for 14 attributes and three CIELab parameters (8 aroma, 6 flavor, and 1 mouthfeel attribute, 3 color parameters) (all $p \leq 0.05$) (data not shown).

With increasing storage temperature several fruit-related attributes (*red fruit*, *grapefruit*, *cherry*) as well as *floral*, *black pepper*, *chemical*, and *fresh veggie* aroma descriptors decreased significantly ($p \leq 0.05$), while *canned veggie*, *earthy*, *molasses/soysauce*, *dried fruit*, *oxidized*, and *brown* aromas and flavors were significantly higher in the samples stored at 40 °C, the highest storage temperature ($p \leq 0.05$) (see Table 4a). Storage temperature affected *bitter* taste as well as *hot* and *viscous* mouthfeel; perception of all three attributes increased with increasing storage temperature ($p \leq 0.05$). Samples stored at lower temperatures were higher in red color (*DA_a**), were less yellow (*DA_b**), and had higher Chroma (*DA_C**) and more hue (*DA_h*), compared to 40 °C samples (Table 4a).

Looking at the packaging effect (Table 4b,c) significant differences between the BIB treatments (*bib, map*) and the bottle treatments (*naco, syco, screw*) were found. All attributes showing a significant packaging effect were scored lower in the two BIB treatments (*bib, map*) compared to the bottle treatments (*naco, syco, screw*), with the exception of *soysauce, dried fruit, oxidized*, and *brown* aroma and flavors, which were higher in the BIB samples. Wines stored in BIB were lighter and less red and had lower Chroma and hue values compared to wines stored in bottles. This is an indication of a more aged wine, as with increasing age red wines tend to lose their red color and become lighter and more transparent. With the exception of one attribute—*grapefruit* aroma, which was significantly higher in the treatments closed with a synthetic closure—the three bottle treatments were not significantly different from each other. This can probably be explained by the less oxygen present in the wine closed with the screw caps during the storage period and is in alignment with Lee et al.,[16] who found the highest scores in *citrous* after 1 week storage at 18 °C for a Cabernet Sauvignon wine when capped with the high absorption capacity oxygen scavenger and natural cork and that this was a significant difference compared to the Cabernet Sauvignon capped with a natural cork but without the O_2 scavenger.

A clear separation among the samples due to the storage temperature was obtained for the aroma, flavor, taste, and mouthfeel attributes, with an explained variance ratio of 74.2% within the first two canonical variates (CV) (Figure 1a). Samples stored at 40 °C were clearly separated from those stored at 10 and 20 °C, with the three 40 °C bottle treatments (*naco, syco, screw*) forming a group along the positive CV 2, and the two 40 °C BIB treatments forming a second group in the bottom right quadrant. Samples stored at 10 °C, which were more similar to each other than the samples stored at 20 °C, were highly correlated to *fresh veggie* aroma, *cherry* flavor, *hot* mouthfeel, *red fruit* flavor, and *bitter* taste and were positioned in the bottom left quadrant. The aroma and flavor descriptors *molasses/soy sauce*, *oxidized*, *dried fruit*, *earthy*, *brown*, *canned veggie*, and *viscous* mouthfeel were highly correlated to the 40 °C samples. At this higher storage temperature, BIB treatments were more described by the *dried fruit* and *oxidized* characters, while the bottle treatments were also characterized by *canned veggie*, *earthy*, and *viscous* mouthfeel.

Panelists used aroma and flavor attributes in a similar way, indicated by a close position of the respective aroma and flavor attribute terms (e.g., *canned veggie* aroma and *canned veggie* flavor in the top left quadrant of the variables plot in Figure 1a).

For the color DA a similar separation among the samples due to the storage temperature and packaging type was achieved (Figure 1b). In the CVA, 98% of the total variance ratio was explained within the first two CVs. All samples stored at 10 °C formed a group in the bottom right quadrant and showed a high positive correlation to Chroma *DA_C**, red color *DA_a**, and hue *DA_h*. Located together with these wines were also three of the 20 °C samples (*bib20*, *map20*, *naco20*), while the remaining two 20 °C samples (*screw20*, *syco20*) were positioned a bit further up along the second canonical variate CV 2 and in between the 10 °C group and the 40 °C bottle samples in the top right quadrant. The latter samples showed higher yellow color and were lighter, thus being positively correlated to *DA_b** and *DA_L**. The last two samples (*bib40*, *map40*) were positioned in the bottom left quadrant and were characterized by their negative correlation to red color, Chroma, and hue.

Table 3. List of Detected Volatile Compounds with Their Identification Features Using the Method of Hjelmeland et al.[50] [a]

	compound	CAS #	RI_{lit} [b]	RI_{calc}	SIM ions
X1	ethyl acetate	141-78-6	907	915	43, 61, 88
X2	ethyl-2-methyl propanoate	97-62-1	955	960	43, 71, 116
X3	ethyl butanoate	105-54-4	1028	1022	116, 88, 71
X4	ethyl 2-methylbutanoate	7452-79-1	1050	1038	57, 102, 130
X5	ethyl 3-methylbutanoate	108-64-5	1069	1055	85, 88, 130
X6	methyl-2-propanol	78-83-1	1099	1101	43, 74, 55
X7	isoamyl acetate	123-92-2	1132	1126	55, 87, 130
X8	methyl-3-propanol	123-51-3	1205	1216	57, 70, 88
X9	ethyl hexanoate	123-66-0	1220	1238	88, 99, 144
X10	hexyl acetate	142-92-7	1270	1278	43, 84, 144
X11	hexanol	111-27-3	1360	1366	56, 69, 102
X12	ethyl octanoate	106-32-1	1436	1443	88, 101, 172
X13	1-octen-3-ol	3391-86-4	1449	1464	57, 72, 128
X14	vitispirane 1		1515	1526	177, 192, 93
X15	vitispirane 2		1522	1529	177, 192, 93
X16	2-undecanone (IS)	112-12-9	1598	1604	58, 71, 170
X17	ethyl decanoate	110-38-3	1636	1645	88, 101, 200
X18	diethyl succinate	123-25-1	1666	1689	56
X19	2-phenethyl acetate	103-45-7	1829	1814	91, 104, 121
X20	2-phenethyl alcohol	60-12-8	1925	1916	65, 103, 122
X21	acetic acid[c]	64-19-7	1450	1461	
X22	isovaleric acid[c]	503-74-2	1665	1703	
X23	octanoic acid[c]	124-07-2	2083	2086	
X24	decanoic acid[c]	334-48-5	2361	2253	

[a] RI, retention index; SIM, selected ion monitoring. [b] Literature values RI on a DB-WAX column were obtained from refs 65−67. [c] Areas for acids were obtained from the total ion chromatogram (TIC).

Table 4. Means of the Significant Sensory Attributes Together with Tukey's HSD, Separated for (a) the Temperature (*T*) Effect and (b) the Packaging (*P*) Effect for All Five Packaging Types and (c) Averaged over the Three Bottle Treatments and Two BIB Treatments[a]

	(a) storage temperature					(b) packaging type					
	10 °C	20 °C	40 °C	HSD		*naco*	*syco*	*screw*	*bib*	*map*	HSD
redFruitA	3.0 a	2.8 a	1.9 b	0.5	grapefruitA	1.6 ab	1.8 b	1.6 ab	1.2 b	1.0 b	0.6
grapefruitA	1.7 a	1.5 ab	1.1 b	0.4	freshVegA	2.3 a	1.7 ab	2.4 a	1.4 b	1.6 b	0.7
freshVegA	2.0 ab	2.1 a	1.6 b	0.5	canVegA	1.7 ab	1.6 ab	2.2 a	1.4 b	1.7 ab	0.8
canVegA	1.3 b	1.3 b	2.5 a	0.5	blPepA	1.4 ab	1.4 ab	1.6 a	0.9 c	1.0 bc	0.5
earthyA	1.6 b	1.6 b	2.3 a	0.4	molsoyA	1.6 b	2.1 ab	2.0 ab	2.3 ab	2.5 a	0.8
blPepA	1.4 a	1.4 a	1.0 b	0.3	brFlA	1.5 bc	1.5 bc	1.5 c	2.3 a	2.2 ab	0.7
molsoyA	1.3 b	1.4 b	3.6 a	0.5	drFrtA	1.3 c	1.5 bc	1.7 abc	2.2 a	2.0 ab	0.7
brFlA	1.5 b	1.3 b	2.6 a	0.5	oxidA	1.6 b	1.5 b	1.8 b	2.8 a	3.1 a	0.7
drFrtA	1.4 b	1.5 b	2.3 a	0.4	redFrtF	2.6 ab	3.1 a	2.6 ab	2.4 b	2.1 b	0.7
oxidA	1.4 b	1.3 b	3.8 a	0.5	grapefruitF	1.6 ab	2.1 a	1.8 ab	1.3 b	1.4 b	0.6
chemA	2.6 a	2.2 ab	2.0 b	0.5	woodyF	1.6 ab	1.5 ab	2.1 a	1.6 ab	1.5 b	0.6
floralA	1.5 a	1.7 a	1.0 b	0.4	blPepF	1.0 ab	1.0 ab	1.3 a	0.8 b	0.9 b	0.4
redFruitF	3.0 a	2.7 a	1.9 b	0.4	molsoyF	1.7 b	1.7 b	1.7 b	2.2 ab	2.5 a	0.7
cherryF	2.7 a	2.8 a	2.0 b	0.5	brFlF	1.2 b	1.3 b	1.6 ab	1.8 ab	2.0 a	0.6
grapefruitF	1.7 ab	1.8 a	1.4 b	0.4	drFrtF	1.5 b	1.7 b	1.8 ab	2.4 a	2.0 ab	0.6
canVegF	0.8 b	0.7 b	1.4 a	0.4	oxidF	1.5 b	1.5 b	1.8 b	2.7 a	2.9 a	0.7
earthyF	1.1 b	1.0 b	1.7 a	0.3	DA_L*	42.9 ab	42.8 ab	43.7 a	41.9 ab	41.7 b	2.0
blPepF	1.2 a	1.0 ab	0.9 b	0.2	DA_a*	36.8 a	35.3 a	36.3 a	32.8 b	32.9 b	1.9
spiceF	1.6 ab	1.4 b	1.7 a	0.3	DA_C*	40.0 a	38.8 ab	39.4 a	37.0 b	37.0 b	2.0
molsoyF	1.3 b	1.6 b	3.0 a	0.5	DA_h	1.2 a	1.2 a	1.2 a	1.1 b	1.1 b	0.0
brFlF	1.5 b	1.2 b	2.1 a	0.4		(c) packaging type					
drFrtF	1.5 b	1.6 b	2.5 a	0.4		bottle	bag-in-box	HSD			
oxidF	1.3 b	1.1 b	3.8 a	0.5	blPepA	1.5 a	1.0 b	0.5			
bitterT	2.8 ab	2.5 b	3.2 a	0.4	brownFlavA	1.5 b	2.2 a	0.7			
hotMF	3.9 b	3.6 b	4.3 a	0.5	oxidizedA	1.7 b	2.9 a	0.7			
viscMF	3.0 b	3.0 b	3.5 a	0.4	oxidizedF	1.6 b	2.8 a	0.7			
DA_a*	37.5 a	36.9 a	30.0 b	1.3	DA_a*	36.2 a	32.8 b	1.9			
DA_b*	14.5 b	14.5 b	17.5 a	1.0	DA_C*	39.4 a	37.0 b	2.0			
DA_C*	40.4 a	39.8 a	35.2 b	1.3	DA_h	1.2 a	1.1 b	0.0			
DA_h	1.2 a	1.2 a	1.0 b	0.0							

[a]Rows sharing the same letter are not significantly different from each other ($p \leq 0.05$) (A, aroma; F, flavor). For sample and variable codes refer to Table 1 and Table 2.

Physical and Chemical Analyses. After the 6-month storage period all enological parameters but pH (TA, VA, ethanol, free and total SO_2) differed significantly among the 15 treatments (all $p \leq 0.05$, Table1). Compared to the initial concentrations, determined by the donating winery prior to filling and bottling of the samples, a strong decrease in free and total SO_2 was observed (from initial 54 mg/L to at or below 30 mg/L and from initial 131 mg/L to 109 mg/L or below), with no free SO_2 detectable ($p \leq 0.05$) in the samples stored at 40 °C. It seems that storage temperature had the larger effect on both free and total SO_2, as we could not find significant differences at the lower temperatures among the different packaging types. Kwiatkowski and co-workers found in their study, conducted over a period of 24 months, that Cabernet Sauvignon wine stored under natural cork, synthetic cork, and screw cap with a medium headspace level of 16 mL did not differ significantly in free and total SO_2 levels after 6 months when stored at around 16 °C, while the extreme low and high headspace levels differed significantly throughout the whole storage period.[3] In other studies[3,19,29,30] significant differences in free and/or total SO_2 levels among different packages were found, e.g., comparing glass bottles to BIB and PET bottles after 12 months at an unknown temperature,[29] glass bottles to PET bottles after 7 months at an unknown temperature,[30] and different oxygen exposure.[19]

Within the treatments, bottle samples stored at 40 °C showed significantly less titratable acidity (TA) compared to their cooler stored counterparts. This effect was not observed for the two BIB treatments, which did not differ significantly at any storage temperature from each other and remained at the initial TA level.

A different behavior was found for volatile acidity (VA) values, which were not statistically different from each other, with the exception of the natural cork sample stored at 10 °C (*naco10*), which showed significantly lower amounts of VA ($p \leq 0.05$). No storage temperature effect was found for both synthetic cork and screw cap closures, as well as the BIB treatments, indicating a similar behavior, independent of storage temperature and wine packaging type, with the exception of the natural cork closures.

In contrast to the sensory results where the trained panel found a significant increase in *hot* mouthfeel with increasing storage temperature, the ethanol levels did not differ significantly among the samples with the exception of the two BIB samples stored at 40 °C (*bib40*, *map40*), which had significantly lower ethanol content ($p \leq 0.05$). We observed a similar behavior in our earlier study on Chardonnay, where the samples stored in BIB at 40 °C had significantly lower levels of ethanol, and speculated that during the storage the ethanol migrates into

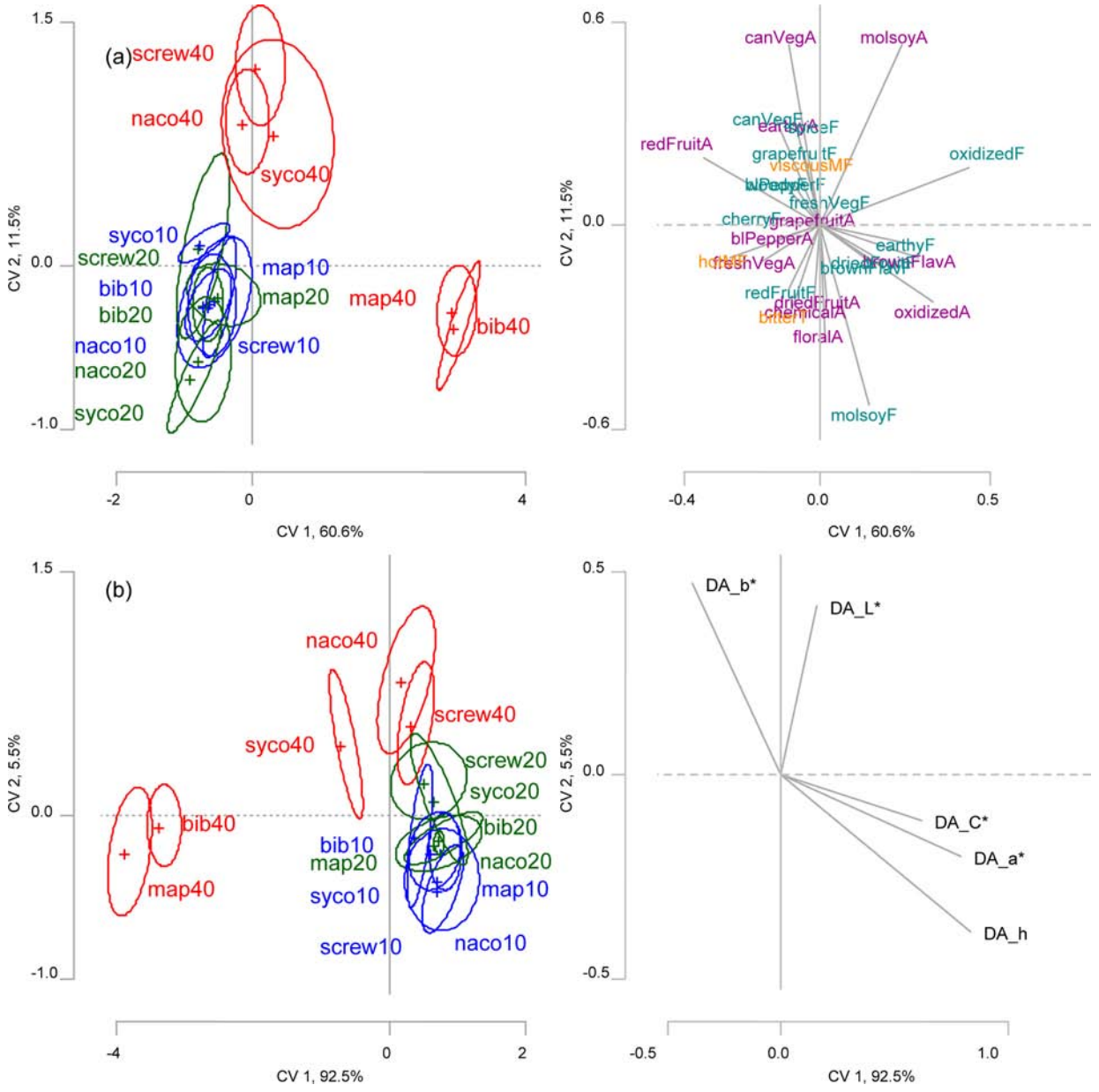

Figure 1. (a) Canonical variate analysis plots for the aroma (in purple), flavor (in turquoise), taste and mouthfeel (both in orange) attributes. (b) Canonical variate analysis plots for the sensory color evaluation. Samples are color coded according to their storage temperature (blue, 10 °C; green, 20 °C; red, 40 °C). Sample and variable codes are explained in Table 1. Circles around the product means represent the 95% confidence intervals according to ref 51.

the plastic bag or took part in chemical reactions. A strong indicator for the former explanation could be the observation by Peyches-Bach and co-workers,[60] who found that a food grade polyethylene film (similar to the one used in this study) was able to take up to 3.89 kg/m^3 ethanol from a 12 v % ethanolic solution within 21 days of contact. On the basis of this result we speculate that the higher storage temperature used in our study facilitated this phenomenon even more.

All five instrumentally measured color parameters differed significantly among the samples ($p \leq 0.05$) (Table 5). A packaging type differentiation was observed between the bottle and BIB treatments for red color and lightness: While for the three bottle treatments (*naco, syco, screw*) lightness L^* and red color a^* decreased with increasing storage temperature, the opposite was observed in the two BIB treatments (*bib, map*), which were significantly lighter and less red in color when stored at 40 °C ($p \leq 0.05$). We believe that these observations reflect different wine development stages, due to different oxygen levels present in the different packaging types. The effect of OTR on the color changes in red wine was shown by Kwiatkowski and co-workers,[3] who found the highest a^* and lowest L^* values in Cabernet Sauvignon with the highest oxygen levels after a storage period of 6 months at 16 °C, while the same wine stored with minimal headspace was least red and the lightest in color throughout the storage period of 24 months.

The changes in yellow color, as well as hue, expressed as b^* and h values, differed significantly only due to changes of the storage temperature, independent of the packaging, with increasing yellow color, and decreasing hue with increasing storage temperature. For Chroma (C^*), samples did not differ significantly

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Table 5. Means and Tukey's Honestly Significant Differences (HSD) for All Instrumental Color and Polyphenol Measurements, Including CIELab Color Space (*L, *a**, *b**, *C**, *h*), and Parameters According to Somers and Evans[35−37,47] As Well As Harbertson and Adams[14,33,34,63,64] [a]**

	naco10	*naco20*	*naco40*	*syco10*	*syco20*	*syco40*	*screw10*	*screw20*	*screw40*	*bib10*	*bib20*	*bib40*	*map10*	*map20*	*map40*	HSD
*L** [−]	38.9 e	39.3 d	37.8 h	38.9 e	38.9 e	36.6 i	39.9 c	40.0 c	38.5 f	38.2 g	37.8 h	41.7 a	38.9 e	38.1 g	40.8 b	0.19
*a** [−]	39.5 ab	39.3 ab	29.6 c	39.4 ab	39.3 ab	36.0 b	39.6 ab	39.2 ab	37.0 ab	40.8 a	40.6 a	31.4 c	40.2 ab	40.3 ab	29.9 c	4.48
*b** [−]	19.4 efghi	19.2 ghij	24.0 c	19.5 efg	19.7 e	24.1 c	18.9 j	19.1 hij	23.5 d	19.6 ef	19.3 fghi	33.4 a	19.0 ij	19.5 efgh	32.6 b	0.38
*C** [−]	44.0 a	43.7 a	38.3 b	44.0 a	44.0 a	43.3 a	43.8 a	43.6 a	43.8 a	45.3 a	44.9 a	45.8 a	44.5 a	44.7 a	44.3 a	3.53
h [−]	1.1 a	1.1 a	0.9 c	1.1 a	1.1 a	1.0 b	1.1 a	1.1 a	1.0 b	1.1 a	1.1 a	0.8 d	1.1 a	1.1 a	0.7 d	0.07
CA1 [au]	0.673 abc	0.663 abc	0.603 bcd	0.677 ab	0.690 ab	0.603 bcd	0.633 abcd	0.690 ab	0.603 bcd	0.693 a	0.660 abc	0.553 d	0.620 abcd	0.707 a	0.587 cd	0.089
CA2 [au]	0.150 d	0.157 d	0.413 b	0.160 d	0.163 d	0.430 b	0.130 d	0.157 d	0.350 c	0.153 d	0.170 d	0.660 a	0.133 d	0.170 d	0.610 a	0.058
DIA [%]	13 b	13 b	36 a	13 b	13 b	43 a	13 b	13 b	35 a	12 b	14 b	n.d. c	15 b	13 b	n.d. c	9.2
I [mg/L]	257 abc	240 bcde	45 fg	236 a	235 de	39 f	267 cde	231 cde	64 g	247 abcd	220 e	n.d. h	259 ab	224 e	n.d. h	22.6
CD [au]	7.7 abc	7.6 bc	8.3 ab	7.4 c	7.5 bc	8.5 a	7.3 c	7.3 c	8.0 abc	7.4 bc	7.7 bc	7.6 bc	7.7 abc	7.5 bc	7.8 abc	0.84
cCD [au]	9.3 a	9.1 ab	8.9 ab	9.2 ab	8.9 ab	8.9 ab	8.8 ab	8.6 abcd	8.4 bcd	8.9 ab	9.3 ab	7.8 cd	8.8 abc	8.7 abcd	7.7 d	0.98
hS [−]	0.797 k	0.827 hi	1.210 d	0.813 j	0.827 hi	1.230 c	0.797 k	0.830 gh	1.130 e	0.817 ij	0.843 f	1.470 a	0.810 j	0.840 fg	1.353 b	0.013
tP [au]	51.9 ab	52.3 a	51.8 ab	53.7 a	52.6 a	52.4 a	50.6 ab	50.4 ab	49.0 abc	49.1 abc	50.1 abc	46.2 bc	50.1 abc	49.6 abc	44.3 c	5.93
rPig [au]	2.633 b	2.567 b	2.933 a	2.600 b	2.633 b	3.000 a	2.267 c	2.533 b	2.667 b	2.567 b	2.667 b	2.533 b	2.300 c	2.633 b	2.600 b	0.229
IRP [mg/L]	1120 a	1120 a	1089 a	1101 a	1116 a	1082 a	1137 a	1143 a	1117 a	1081 a	1095 a	955 b	1120 a	1104 a	907 b	94.7
SPP [−]	1.81 efg	1.74 fgh	1.9 cdef	1.99 bcd	1.97 bcde	2.2 a	1.81 efg	1.83 defg	2.12 ab	1.87 cdef	2.03 abc	1.69 gh	1.88 cdef	1.91 cdef	1.6 h	0.17
LPP [−]	1.14 def	1.16 def	1.72 b	0.93 f	0.96 ef	1.59 bc	0.98 ef	1.01 ef	1.42 cd	1.23 de	1.11 ef	2.44 a	0.98 ef	1.00 ef	2.49 a	0.28
tT [mg/L]	400 cde	366 fg	327 h	388 def	364 fg	336 gh	419 bcd	375 ef	314 h	437 b	421 bc	544 a	423 bc	394 cdef	561 a	32.4
tA [mg/L]	435 a	406 ab	148 c	434 a	391 ab	131 cd	430 a	385 ab	154 c	432 a	370 b	92 d	412 ab	378 b	94 d	52

[a] Rows sharing the same letter are not significantly different from each other ($p \leq 0.05$). For sample and variable codes refer to the Materials and Methods section and Table 1.

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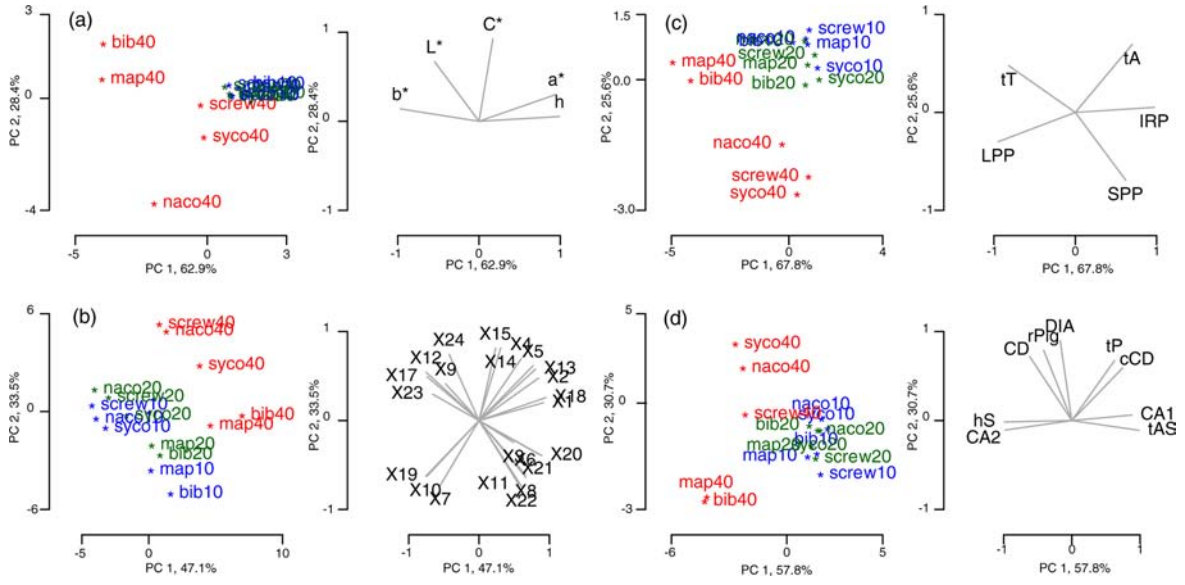

Figure 2. PCA plots for the samples using (a) instrumental color measurements, (b) volatile profile data, (c) Harbertson–Adams assay, and (d) Somers–Evans assay values. Samples are color-coded according to their storage temperature (blue, 10 °C; green, 20 °C; red, 40 °C). All sample and variable codes are explained in Tables 1, 3, and 5.

from each other with the exception of *naco40*, which was significantly lower in Chroma. An explanation for this is that the lowest a^* value was observed for *naco40*; this affects the Chroma value due to its calculation from a^* and b^* values.

All these observations were also reflected in the PCA shown in Figure 2a. All samples were separated based on their storage temperatures, with virtually no differences between different packaging types stored at 10 and 20 °C. Within the first two principal components (PC) 91.3% of the total variance was explained (PC 1 62.9%, PC 2 28.4%), mainly due to four (L^*, a^*, b^*, h) out of the five color parameters. Chroma C^* nearly exclusively explained PC 2. Both 10 and 20 °C samples show a high positive correlation to red color a^* and hue h. For the 40 °C samples, both BIB samples (*bib40*, *map40*) were positioned together in the top left quadrant, mainly characterized by their yellow color b^* and light color L^*. The screw cap and synthetic cork samples (*syco40*, *screw40*) are located around the center of the product plot, with intermediate values in L^*, a^*, b^*, and h. The last sample, *naco40*, is located in between the two 40 °C sample groups along PC 1 and showed a negative correlation to Chroma C^*.

Twenty-four volatile compounds were detected in the samples, and 23 volatiles differed significantly ($p \leq 0.05$) among all samples and were used in the subsequent PCA (data not shown). Most volatiles differed in concentration due to both significant packaging and temperature effects, with the exception of seven compounds showing only a significant packaging effect ($p \leq 0.05$); that is, the alcohols *X6*, *X8*, *X11*, and *X20*, ethyl hexanoate *X9*, and the two organic acids *X21* and *X22* were present in different amounts depending on the packaging type. For these volatiles with a significant packaging effect, the amounts in the two BIB treatments (*bib*, *map*) differed from the bottle concentrations, with higher concentrations in the *bib* and *map* samples except for ethyl hexanoate (*X9*). In a comparative bottle closure study with Cabernet Sauvignon, Blake et al.[21] found similarly higher concentrations of phenylethyl acetate, decanoic, octanoic, and hexanoic ethyl esters, and isoamyl acetate in the Tetrapak and screw cap samples compared to the natural and synthetic corks, after 12 months. Additionally, significant changes in some of these volatiles were reported also by Lee and co-workers [16] for Cabernet Sauvignon, differing in oxygen levels during a 7-day shelf-life study. The wine stored with a natural cork had significantly lower levels of only 2-methyl-1-propanol and hexanol than the same wine stored with a high-capacity oxygen scavenger and a natural cork. The wine with more oxygen exposure also showed higher concentrations in 3-methyl-1-propanol, 2-phenylethanol, and ethyl hexanoate ($p \leq 0.05$), in good agreement with our findings except for the ethyl ester. Similarly, Mentana et al.[30] found significant differences after 7 months between PET and glass bottles in hexanol and isovaleric acid, but not in acetic acid, 2-phenylethanol, 2-methyl-1-propanol, or ethyl hexanoate concentrations.

All other compounds showed a significant temperature effect ($p \leq 0.05$) and either increased (ethyl esters *X1*, *X2*, *X3*, *X4*, *X5*, and *X18*, 1-octen-3-ol *X13*, and both vitispirane compounds *X14* and *X15*) or decreased (acetates *X7*, *X10*, and *X19*, ethyl esters *X12* and *X17*, and octanoic acid *X23*) with increasing storage temperature independent of the packaging type. However, for some compounds a faster decline or incline was observed in some packaging types (e.g., for the two ethyl esters *X2* and *X17* the concentrations doubled or halved from 10 °C to 40 °C in the synthetic cork samples, while the same compounds changed to a smaller degree in the screw cap samples) (Supplementary Table 1).

For 12 compounds an additional significant interaction between the packaging and temperature treatments indicated different degradation and/or formation mechanisms depending on the packaging type (*X2–X5*, *X9*, *X12–X15*, *X17*, *X23*, *X24*) (see Supplementary Table 1). These compounds include various ethyl esters, alcohols, and organic acids, and the observed interaction is most likely a result of flavor scalping phenomena and/or faster oxidation in the BIB treatments, which are sped up at the higher storage temperatures.

All significant volatiles ($p \leq 0.05$) were included to produce the PCA plots shown in Figure 2b. Over 80% of the total variance could be explained within the first two PCs. Samples were separated due to both storage temperature and packaging type. All 10 °C samples are located at the bottom of the graph,

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while the 40 °C samples were positioned in the top right quadrant and the 20 °C samples are in between these two groups. Additionally, all bottle treatments (*naco*, *syco*, *screw*) were separated from the two BIB treatments (*bib*, *map*) for all three storage temperatures.

The 10 and 20 °C *map* and *bib* samples in the bottom left corner were highly correlated to the volatile acetates *X7*, *X10*, and *X19*, while the 10 and 20 °C bottle samples (*naco*, *syco*, *screw*) showed an additional positive correlation to the ethyl esters *X9*, *X12*, and *X17* and octanoic acid *X23*. At the highest storage temperature of 40 °C all samples showed a positive correlation to all remaining compounds, including various ethyl esters, alcohols, ethyl acetates, and organic acids, some of them known aging compounds such as diethyl succinate (*X18*), 1-octen-3-ol (*X13*), vitispiranes 1 and 2 (*X14*, *X15*), 2-phenethyl alcohol (*X20*), and acetic acid (*X21*).[7,16,28,61]

General polyphenol patterns were determined using two different assays. For the 14 parameters determined by the assays a significant *wine* effect was found in the MANOVA ($p \leq 0.05$). In the subsequent ANOVAs all parameters were found to differ significantly ($p \leq 0.05$) among the samples and were included in the PCA (Figure 2c,d). Significant temperature (*T*) effects ($p \leq 0.05$) were found for all parameters except total tannins *tT* and small polymeric pigments *SPP* in the Harbertson–Adams assay. Further, with the exception of chemical age 1 *CA1*, color density *CD*, and total anthocyanins *tA*, all parameters showed a significant packaging (*P*) effect ($p \leq 0.05$). For 12 out of the 14 variables a significant interaction between packaging type and storage temperature (*P:T*) ($p \leq 0.05$) was found (all but total phenols *tP* in the Somers assay and total anthocyanins *tA* in the Harbertson–Adams assay). These findings are also reflected when comparing the means and Tukey's multiple comparisons (Table 5).

For the bottle treatments, an increase in *CA2*, *DIA*, *CD*, *hS*, *rPig*, *SPP*, and *LPP* values was observed with increasing storage temperature, for which *DIA*, *CD*, *hS*, *rPig*, and *LPP* showed some significant differences among the three closures and storage temperatures ($p \leq 0.05$). The parameters *CA1*, *tAS*, *cCD*, *tP*, *IRP*, *tT*, and *tA* showed a negative correlation with increasing storage temperature, with only small and not significant differences in *CA1*, *cCD*, *tP*, and *IRP* ($p \leq 0.05$).

For the two BIB treatments, significantly lower levels in *CA1*, *DIA*, *tAS*, *cCD*, *IRP*, *SPP*, and tA were the result of the higher storage temperature, while the storage at 40 °C significantly increased the parameters *CA2*, *hS*, *rPig*, and *LPP* ($p \leq 0.05$). No significant differences were found among the BIB treatments in color density (*CD*) and total phenols (*tP*) ($p \leq 0.05$).

The graphical sample representations obtained by PCA are shown for both assays in Figure 2c,d. For the Harbertson–Adams data set 93.4% of the total variance could be explained within the first two principal components. A separation based on the storage temperature was found, with all 40 °C samples on the plot's left-hand side showing a positive correlation to large polymeric pigments *LPP* and total tannins *tT*, while the 10 °C samples positioned in the top right quadrant were characterized by high values in total anthocyanins *tA* and iron-reactive phenolics *IRP*. The 20 °C samples were positioned in between the two groups in the top middle part of the product plot and showed a negative correlation to small polymeric pigments *SPP*. Small polymeric pigments *SPP* have been shown to not precipitate with protein, while *LPP* do. Due their role as the stable form of red wine color, they have been shown to correlate positively to aging.[33] Comparing *SPP* and *LPP* in grapes and wines made thereof, it was shown that both *SPP* and *LPP* are present in higher amounts in the wine and that with aging *LPP* is the preferred form.[32] From previous studies it is known that with increasing storage time and/or oxygen exposure anthocyanin levels decrease, due to being the primary oxidation target compounds,[3,13,21,25] while either no effect or an increase in total phenols was observed with higher oxygen exposure.[3,13]

In contrast to that, the PCA for the Somers assay data was not able to separate the samples according to their storage temperatures as clearly as in the Harbertson–Adams PCA (Figure 2c), as the 10 and 20 °C samples were positioned all together in the bottom right quadrant of the product plot (Figure 2d). Additionally, the two 40 °C BIB samples (*bib40*, *map40*) were grouped in the bottom left corner, away from the three 40 °C bottle samples (*naco40*, *syco40*, *screw40*). In general, this plot resembled the instrumental color plot, where all 10 and 20 °C samples were clustered together, and the 40 °C BIB samples were separated from the 40 °C bottle treatments (Figure 2a).

With increasing storage temperature levels of *CA2*, *hS*, *CD*, *rPig*, and *DIA* increased, thus showing a positive correlation to all 40 °C and some 20 °C samples, while *CA1*, *tAS*, *tP*, and *cCD* correlated positively to the 10 °C and some 20 °C samples on the right-hand side of the plot (Figure 2d).

Correlation of Sensory to Chemical and Instrumental Variables Data Using Partial Least Squares (PLS) Regression. In a last step, PLS regression was used to correlate the 33 aroma, flavor, taste, mouthfeel, and color sensory variables with the 48 chemical and instrumental parameters. The PLS model was evaluated using leave-one-out cross-validation, and for all sensory attributes minimal root-mean-square error of prediction values were obtained after two latent vectors (LVs), explaining a total of 71.2% of the variance (data not shown). Product and correlation plots with both predicting and predicted variables are shown in Figure 3.

Similar to all other product plots, a clear separation of the samples due to the storage temperature was obtained, with the 10 °C samples showing a higher similarity to the 20 °C samples than to the 40 °C samples. Among the 40 °C samples, the two BIB treatments (*bib40*, *map40*) were positioned to the very right of the first latent vector LV 1, while the three bottle treatments (*naco40*, *syco40*, *screw40*) were located along the negative second latent vector LV 2. The samples stored at 10 and 20 °C were highly positively correlated to *red fruit*, *fresh veggie*, *black pepper*, *chemical*, *cherry*, and *floral* aromas and flavors, *bitter* taste, and the perceived color values hue *DA_h*, Chroma *DA_C**, and red color *DA_a**. These sensory attributes were strongly correlated to the volatile acetates *X7*, *X10*, and *X19* and ethyl decanoate *X17*, the total anthocyanin values from both assays *tA* and *tAS*, chemical age 1 *CA1*, corrected color density *cCD*, iron-reactive phenolics *IRP*, total phenols *tP*, ethanol content *EtOH*, free and total SO_2 *fSO2* and *tSO2*, and the instrumental color measurements of hue *h* and red color *a**, as well as the oxygen consumption parameters *auc_HS*, *auc_DO*, and *auc_TPO* and titratable acidity *TA*. In agreement with our findings on the shelf life of Chardonnay[10] were all three single-value oxygen consumption values, obtained from the area under the oxygen consumption curve (*auc*), positively correlated to the wines stored at 10 °C, indicating that the larger the *auc*, the less oxygen consumed by the wine.

Similar to our study, various esters were found previously to be positively correlated and involved in perceived fruitiness and floral notes in red wine.[7,16,21] The *chemical* aroma used by the panelist in the study included the aroma perception of ethanol;

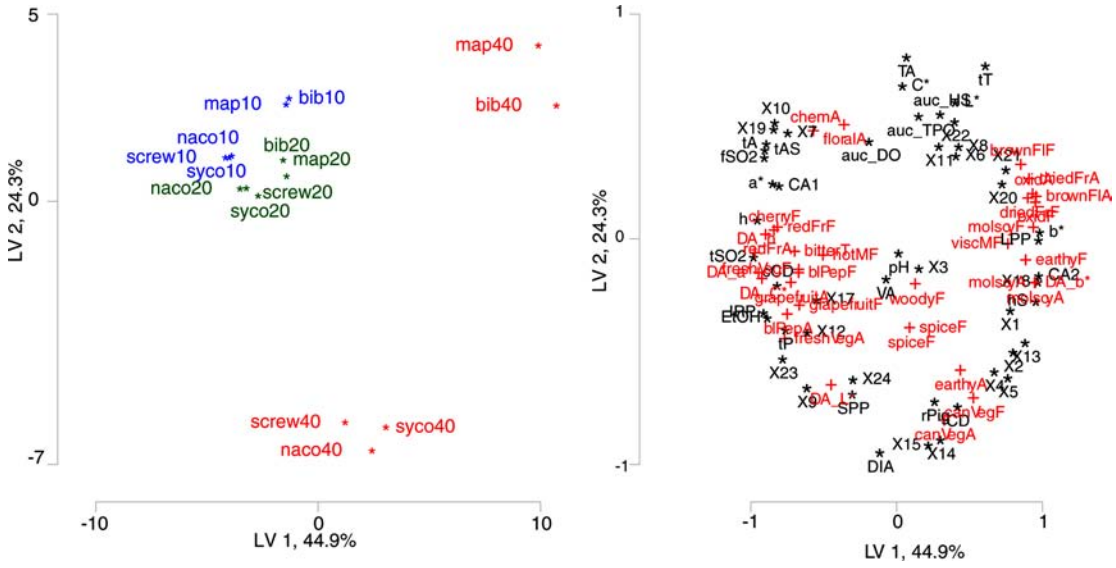

Figure 3. Partial least squares (PLS) regression with product plot (left) and correlation plot (right). Samples are color-coded according to their storage temperature (blue, 10 °C; green, 20 °C; red, 40 °C). Sensory attributes are written in red and marked with a cross, while chemical and physical variables are in black and marked with an asterisk (samples and variables codes are explained in Tables 1,3, and 5).

thus, the positive correlation of *chemical* to the ethanol content *EtOH* is not surprising. However, the correlation of *fresh veggie* and *black pepper* to specific volatiles is most likely more accidental than causal. Robinson et al.[62] reports a positive correlation between the protein precipitation assay and perceived bitterness, similar to our PLS model. All polyphenol parameters as well as the instrumental color space values are well correlated to the perceived red, intense, and full color (*DA_a**, *DA_C**, *DA_h*) of the wines stored at 10 and 20 °C. Kwiatowski and co-workers[3] described a positive correlation between total tannin concentration, red color *a**, color density, and Chroma and found that these parameters were highest in wines filled with the largest headspace, while wines filled with the lowest headspace were positively correlated to total anthocyanin levels, lightness, and free and total SO_2 and negatively to red color *a**, Chroma *C**, and total tannin levels.

The 40 °C bottle samples (*naco40*, *syco40*, *screw40*) in the bottom of the plot were highly correlated to the sensory variables lightness *DA_L**, *canned veggie* aroma and flavor, and *earthy* aroma. These sensory attributes showed a high positive correlation to the two isobutyl and hexyl ethyl esters (*X4*, *X5*, *X9*), vitispiranes 1 and 2 (*X14*, *X15*), and octanoic and decanoic acids (*X23*, *X24*), as well as to the polyphenol values degree of ionized anthocyanins *DIA*, small polymeric pigments *SPP*, SO_2-resistant pigments *rPig*, and color density *CD*. Vitispirane was previously reported to correlate with heat-damaged wines,[7] while increased octanoic acid levels were reported in packages with higher OTR[30] and higher oxidation levels,[18] and Lee et al.[16] and Ferreira and Juan[26] reported higher levels in ethyl-3-methyl butanoate in aged wines and oxidized Tempranillo wines.[18]

The sensory attributes *dried fruit*, *molasses/soy sauce*, *oxidized*, *brown* aroma and flavors, and *earthy* flavor characterized the 40 °C BIB samples (*bib40*, *map40*) and were best predicted by the volatile compounds ethyl acetate (*X1*), the alcohols *X6*, *X8*, *X11*, and *X20*, diethyl succinate (*X18*), and the volatile acids *X21* and *X22*. The highest scores in *viscous* mouthfeel could be attributed to changes in polyphenol composition, as the PLS suggests a correlation between the sensory perception of viscosity and large polymeric pigments *LPP* and total tannins *tT*. We speculate that the panel might have used the viscosity term to describe effects of a smoother/silkier mouthfeel due to the absence of astringency, a term that turned out to be not significant in the DA ($p \leq 0.05$).

The hue determined with the Somers assay *hS*, chemical age 2 *CA2*, and the instrumental measurement of yellow color *b**, lightness *L**, and Chroma *C** were closely positioned to the sensorially determined yellow color (*DA_b**), while the sensory panel rated the bottle treatments stored at 40 °C lighter in color than the BIB samples stored at the same temperature. We believe that this can be related to the formation of precipitates in the *bib40* and *map40* samples, which were not accounted for in the instrumental color measurements, but detected by the panel. The instrumental color space values are in good agreement with the literature, as Lopes[17] recently reported that with increasing storage time *b** and *C** increase over time, with maximum values in wines closed with synthetic corks, while the lightest wines were obtained when closed with a screw cap with tin liner or stored in an ampule.

Some variables were positioned in the center of the correlation loadings plot, an indication of their lesser importance in describing the differences among the wines. These variables were *woody* and *spice* flavor as well as volatile acidity *VA*, pH, and ethyl butanoate *X3*.

In summary, Cabernet Sauvignon wine ages differently depending on the storage conditions such as temperature and packaging type. Depending on the combination of storage temperature and packaging, sensorially detectable differences in aroma, taste, mouthfeel, and color attributes were found by a trained DA panel. Additionally, these sensory changes could be correlated to changes in the volatile composition, polyphenol pattern, and various enological parameters such as ethanol, titratable acidity, and sulfur dioxide concentration.

Changes in color can be detected similarly well with either a trained panel or a chromameter; however, the panel was able to evaluate the formation of precipitates in the wine stored in BIB at 40 °C, which led to a darker color, while the chromameter did not detect that decrease in lightness. With the exception of precipitate formation in the *bib40* and *map40* samples, wines

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that received the highest oxygen amounts and storage temperature were much lighter, less red, and more brown-yellow wine at the end of the 6-month storage period, compared to their counterparts stored at 10 °C. These changes in color and polyphenols, respectively, were also detected with the two employed spectrophotometric assays. With increasing storage temperature both assays measured reduced concentrations in total phenols and total anthocyanins, while total tannin, degree of ionized anthocyanins, and color density increased. Both assays explained the total variance with over 85% within the first two PCs, but the protein precipitation assay discriminated slightly better among the 10 and 20 °C samples, mostly due to differences in IRP, while the color assay by Somers and Evans produced product plots very similar to the instrumental color space measurements, with around 5% less variance explained within the first two PC dimensions.

Various volatile compounds differed significantly among the samples, with the largest relative concentration changes in acetates, organic acids, and alcohols, in good agreement with previous literature reports, with some being well correlated to specific sensory attributes too, e.g., various acetates correlated to cherry and fruit aromas and flavors.

All used sensory, chemical, and physical methods were able to detect significant differences among the wines due to the storage temperature and packaging configuration. The effect of storage temperature was more prominent than the packaging effect, and no differences were found among the different packaging types for the two lower storage temperatures of 10 and 20°. The packaging type discriminated only at the highest storage temperature of 40 °C. At this storage temperature, all wines showed oxidized characters, independent of the packaging, but to a varying degree, with the highest degree in oxidation characters in the Cabernet Sauvignon stored in BIB packages at the highest storage temperature.

We showed that elevated storage temperatures could be a valuable tool for wine packaging screening and for testing new and improved wine packaging types under the worst conditions, which are unfortunately not unrealistic, as shown in ref 5.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Internal standard-normalized area means of detected volatile compounds measured with HS-SPME-GC-MS together with standard deviations and mean square errors (Supplementary Table 1). This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hhopfer@ucdavis.edu. Phone: +1 530 752 9356.

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■ REFERENCES

(1) Waters, E. J.; Peng, Z.; Pocock, K. F.; Williams, P. J. The role of corks in oxidative spoilage of white wines. *Aust. J. Grape Wine Res.* **1996**, *2*, 191−197.

(2) Caloghiris, M.; Waters, E. J.; Williams, P. J. An industry trial provides further evidence for the role of corks in oxidative spoilage of bottled wines. *Aust. J. Grape Wine Res.* **1997**, *3*, 9−17.

(3) 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.

(4) Skouroumounis, G. K.; Kwiatkowski, M. J.; Francis, I. L.; Oakey, H.; Capone, D. L.; Duncan, B.; Sefton, M. A.; Waters, E. J.; Peng, Z. 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. *Aust. J. Grape Wine Res.* **2005**, *11*, 369−377.

(5) Butzke, C. E.; Vogt, E. E.; Chacon-Rodriguez, L. Effects of heat exposure on wine quality during transport and storage. *J. Wine Res.* **2012**, *23*, 15−25.

(6) Zraly, K. *Windows on the World Complete Wine Course*, 2007 ed.; Sterling: New York, NY, 2006.

(7) Robinson, A. L.; Mueller, M.; Heymann, H.; Ebeler, S. E.; Boss, P. K.; Solomon, P. S.; Trengove, R. D. Effect of Simulated Shipping Conditions on Sensory Attributes and Volatile Composition of Commercial White and Red Wines. *Am. J. Enol. Vitic.* **2010**, *61*, 337−347.

(8) Brajkovich, M.; Tibbits, N.; Peron, G.; Lund, C. M.; Dykes, S. I.; Kilmartin, P. A.; Nicolau, L. Effect of screwcap and cork closures on SO_2 levels and aromas in a Sauvignon Blanc wine. *J. Agric. Food Chem.* **2005**, *53*, 10006−10011.

(9) Kontoudakis, N.; Biosca, P.; Canals, R.; Fort, F.; Canals, J. M.; Zamora, F. Impact of stopper type on oxygen ingress during wine bottling when using an inert gas cover. *Aust. J. Grape Wine Res.* **2008**, *14*, 116−122.

(10) Hopfer, H.; Ebeler, S. E.; Heymann, H. The combined effects of storage temperature and packaging type on the sensory and chemical properties of Chardonnay. *J. Agric. Food Chem.* **2012**, *60*, 10743−10754.

(11) 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.

(12) Fulcrand, H.; Salas, E.; Cheynier, V. Phenolic reactions during winemaking and aging. *Am. J. Enol. Vitic.* **2006**, *57*, 289−297.

(13) Gambuti, A.; Rinaldi, A.; Ugliano, M.; Moio, L. Evolution of phenolic compounds and astringency during aging of red wine: effect of oxygen exposure before and after bottling. *J. Agric. Food Chem.* **2012**.

(14) Harbertson, J. F.; Hodgins, R. E.; Thurston, L. N.; Schaffer, L. J.; Reid, M. S.; Landon, J. L.; Ross, C. F.; Adams, D. O. Variability of tannin concentration in red wines. *Am. J. Enol. Vitic.* **2008**, *2*, 210−214.

(15) McRae, J. M.; Kennedy, J. A. Wine and grape tannin interactions with salivary proteins and their impact on astringency: a review of current research. *Molecules* **2011**, *16*, 2348−2364.

(16) Lee, D.-H.; Kang, B.-S.; Park, H.-J. Effect of oxygen on volatile and sensory characteristics of Cabernet Sauvignon during secondary shelf life. *J. Agric. Food Chem.* **2011**, *59*, 11657−11666.

(17) Lopes, P.; Silva, M. A.; Pons, A.; Tominaga, T.; Lavigne, V.; Saucier, C.; Darriet, P.; Cabral, M.; Teissedre, P.; Dubourdieu, D.; Isvv, O.; De, C. Impact of the oxygen exposure during bottling and oxygen barrier properties of different closures on wine quality during post-bottling. In *Flavor Chemistry of Wine and Other Alcoholic*

Beverages; Qian, M. C.; Shellhammer, T. H., Eds.; ACS Symposium Series, Vol. *1104*, 2012; pp 167−187.
(18) Balboa-Lagunero, T.; Arroyo, T.; Cabellos, J. M.; Aznar, M. Sensory and olfactometric profiles of red wines after natural and forced oxidation processes. *Am. J. Enol. Vitic.* **2011**, *62*, 527−535.
(19) Ugliano, M.; Dieval, J.-B.; Siebert, T. E.; Kwiatkowski, M.; Aagaard, O.; Vidal, S.; Waters, E. J. Oxygen consumption and development of volatile sulfur compounds during bottle aging of two Shiraz wines. Influence of pre- and postbottling controlled oxygen exposure. *J. Agric. Food Chem.* **2012**, *60*, 8561−8570.
(20) Ugliano, M.; Henschke, P. A.; Waters, E. J.; Donadille, D. De; Cazeaux, A. Y.; Wine, A.; Box, P. O.; Osmond, G.; Town, K. Fermentation and post-fermentation factors affecting odor-active sulfur compounds during wine bottle storage. In *Flavor Chemistry of Wine and Other Alcoholic Beverages*; Qian, M. C.; Shelleman, T., Eds.; ACS Symposium Series, Vol. *1104*, 2012; pp 189−200.
(21) Blake, A.; Kotseridis, Y.; Brindle, I. D.; Inglis, D.; Sears, M.; Pickering, G. J. Effect of closure and packaging type on 3-alkyl-2-methoxypyrazines and other impact odorants of Riesling and Cabernet Franc wines. *J. Agric. Food Chem.* **2009**, *57*, 4680−4690.
(22) Silva, M. A.; Jourdes, M.; Darriet, P.; Teissedre, P.-L. Scalping of light volatile sulfur compounds by wine closures. *J. Agric. Food Chem.* **2012**, *60*, 10952−10956.
(23) Caillé, S.; Samson, A.; Wirth, J.; Diéval, 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.
(24) Wirth, J.; Caillé, S.; Souquet, J. M.; Samson, A.; Dieval, J. B.; Vidal, S.; Fulcrand, H.; Cheynier, V. Impact of post-bottling oxygen exposure on the sensory characteristics and phenolic composition of Grenache rosé wines. *Food Chem.* **2012**, *132*, 1861−1871.
(25) Wirth, J.; Morel-Salmi, C.; Souquet, J. M.; Dieval, J. B.; Aagaard, O.; Vidal, S.; Fulcrand, H.; Cheynier, V. The impact of oxygen exposure before and after bottling on the polyphenolic composition of red wines. *Food Chem.* **2010**, *123*, 107−116.
(26) Ferreira, V.; San Juan, F. Flavor of wine. In *Food Flavors*; CRC Press, 2011; pp 269−300.
(27) Polaskova, P.; Herszage, J.; Ebeler, S. E. Wine flavor: chemistry in a glass. *Chem. Soc. Rev.* **2008**, *37*, 2478−2489.
(28) Bueno, M.; Culleré, L.; Cacho, J.; Ferreira, V. Chemical and sensory characterization of oxidative behavior in different wines. *Food Res. Int.* **2010**, *43*, 1423−1428.
(29) Ghidossi, R.; Poupot, C.; Thibon, C.; Pons, A.; Darriet, P.; Riquier, L.; De Revel, G.; Mietton Peuchot, M. The influence of packaging on wine conservation. *Food Control* **2012**, *23*, 302−311.
(30) Mentana, A.; Pati, S.; La Notte, E.; Del Nobile, M. A. Chemical changes in Apulia table wines as affected by plastic packages. *LWT−Food Sci. Technol.* **2009**, *42*, 1360−1366.
(31) De Beer, D.; Harbertson, J. F.; Kilmartin, P. A.; Roginsky, V.; Barsukova, T.; Adams, D. O.; Waterhouse, A. L. Phenolics: a comparison of diverse analytical methods. *Am. J. Enol. Vitic.* **2004**, *55*, 12.
(32) Harbertson, J. F.; Spayd, S. Measuring phenolics in the winery. *Am. J. Enol. Vitic.* **2006**, *57*, 280−288.
(33) Harbertson, J. F.; Picciotto, E. A.; Adams, D. O. Measurement of polymeric pigments in grape berry extracts and wines using a protein precipitation assay combined with bisulfite bleaching. *Am. J. Enol. Vitic.* **2003**, *54*, 6.
(34) Heredia, T. M.; Adams, D. O.; Fields, K. C.; Held, P. G.; Harbertson, J. F. Evaluation of a comprehensive red wine phenolics assay using a microplate reader. *Am. J. Enol. Vitic.* **2006**, *57*, 497−502.
(35) Somers, T. C.; Evans, M. E. Wine quality: correlations with colour density and anthocyanin equilibria in a group of young red wines. *J. Sci. Food Agric.* **1974**, *25*, 1369−1379.
(36) AWRI. Measuring red wine colour using the modified Somers assay, http://www.awri.com.au/industry_support/smart_technologies/modified_somers_colour_measure.pdf (accessed Nov 11, 2011).
(37) Somers, C. T.; Evans, M. E. Spectral evaluation of young red wines: anthocyanin equilibria, total phenolics, free and molecular SO_2, "chemical age". *J. Sci. Food Agric.* **1977**, *28*, 279−287.
(38) Perez-Magarino, S.; Gonzalez-Sanjose, M. L. Application of absorbance values used in wineries for estimating CIELAB parameters in red wines. *Food Chem.* **2003**, *81*, 301−306.
(39) Han, F.-L.; Zhang, W.-N.; Pan, Q.-H.; Zheng, C.-R.; Chen, H.-Y.; Duan, C.-Q. Principal component regression analysis of the relation between CIELAB color and monomeric anthocyanins in young Cabernet Sauvignon wines. *Molecules* **2008**, *13*, 2859−2870.
(40) Liang, Z.; Sang, M.; Fan, P.; Wu, B.; Wang, L.; Yang, S.; Li, S. CIELAB coordinates in response to berry skin anthocyanins and their composition in *Vitis*. *J. Food Sci.* **2011**, *76*, C490−C497.
(41) Shea, P.; Vialis, S.; Vidal, J.-C. Bag-in-Box Cone Meter, http://www.b-i-b.com/bib/web/downloads/O2BIBconeMeterBrochure29Nov2010.pdf (accessed Jan 6, 2012).
(42) Lawless, H. T.; Heymann, H. *Sensory Evaluation of Food: Principles and Practices*; Springer: New York, 2010.
(43) Heymann, H.; Machado, B.; Torri, L.; Robinson, A. L. How many judges should one use for descriptive analysis? *J. Sensory Stud.* **2012**, *27*, 111−122.
(44) International Organization for Standardization ISO 3591: Sensory Analysis - Apparatus - Wine tasting glass, 1977.
(45) Organization de Vin. Method OIV-MA-AS2-11: Determination of chromatic characteristics according to CIELab, 2006.
(46) Boselli, E.; Boulton, R. B.; Thorngate, J. H.; Frega, N. G. Chemical and sensory characterization of DOC red wines from Marche (Italy) related to vintage and grape cultivars. *J. Agric. Food Chem.* **2004**, *52*, 3843−3854.
(47) Somers, T. C.; Ziemelis, G. Spectral evaluation of total phenolic components in *Vitis vinifera*: grapes and wines. *J. Sci. Food Agric.* **1985**, *36*, 1275−1284.
(48) Ough, C. S.; Amerine, M. A. *Methods Analysis of Musts and Wines*, 2nd ed.; J. Wiley: New York, USA, 1988.
(49) Zoecklein, B.; Fugelsang, K. C.; Gump, B. H.; Nury, F. S. *Wine Analysis and Production*; Chapman & Hall: New York, NY, 1995.
(50) Hjelmeland, A. K.; King, E. S.; Ebeler, S. E.; Heymann, H. Characterizing the chemical and sensory profiles of U.S. Cabernet Sauvignon wines and blends. *Am. J. Enol. Vitic.* **2012**.
(51) Owen, J. G.; Chmielewski, M. A. On canonical variates analysis and the construction of confidence ellipses in systematic studies. *System. Zool.* **1985**, *34*, 366−374.
(52) Haenlein, M.; Kaplan, A. M. A beginner's guide to partial least squares analysis. *Understanding Stat.* **2004**, *3*, 283−297.
(53) Mevik, B.-H.; Cederkvist, H. R. Mean squared error of prediction (MSEP) estimates for principal component regression (PCR) and partial least squares regression (PLSR). *J. Chemom.* **2004**, *18*, 422−429.
(54) Abdi, H. Partial least squares (PLS) regression . In *Encyclopedia of Social Sciences Research Methods*; M., L.-B.; Bryman, A., Eds.; Sage Publications: Thousand Oaks, CA, 2003; pp 1−7.
(55) Mevik, B.-H.; Wehrens, R. The PLS package: principal component and partial least squares regression in R. *J. Stat. Software* **2007**, *18*, 1−24.
(56) R Foundation for Statistical Computing. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2011.
(57) Lê, S.; Husson, F. Sensominer: a package for sensory data analysis. *J. Sensory Stud.* **2008**, *23*, 14−25.
(58) Le, S.; Josse, J.; Husson, F. F.; Lê, S. FactoMineR: an R package for multivariate analysis. *J. Stat. Software* **2008**, *25*, 1−18.
(59) Friendly, M. HE plots for Multivariate General Linear Models. *Journal of Computational and Graphical Statistics* **2007**, *16*, 421−444.
(60) Peyches-Bach, A.; Dombre, C.; Moutounet, M.; Peyron, S.; Chalier, P. Effect of ethanol on the sorption of four targeted wine volatile compounds in a polyethylene film. *J. Agric. Food Chem.* **2012**, *60*, 6772−6781.
(61) Francis, I. L.; Newton, J. L. Determining wine aroma from compositional data. *Aust. J. Grape Wine Res.* **2005**, *11*, 114−126.

(62) Robinson, A. L.; Adams, D. O.; Boss, P. K.; Heymann, H.; Solomon, P. S.; Trengove, R. D. The relationship between sensory attributes and wine composition for Australian Cabernet Sauvignon wines. *Aust. J. Grape Wine Res.* **2011**, *17*, 13.
(63) Harbertson, J. F.; Kennedy, J. A.; Adams, D. O. Tannin in skins and seeds of Cabernet Sauvignon, Syrah, and Pinot Noir berries during ripening. *Am. J. Enol. Vitic.* **2002**, *53*, 54−59.
(64) Harbertson, J. F.; Yuan, C.; Mireles, M. S.; Hanlin, R. L.; Downey, M. O. Glucose, fructose and sucrose increase the solubility of protein−tannin complexes and at high concentration, glucose and sucrose interfere with bisulphite bleaching of wine pigments. *Food Chem.* **2013**, *138*, 556−563.
(65) Acree, T.; Arn, H. Flavornet and human odor space gas chromatography - olfactometry (GCO) of natural products, http://www.flavornet.org.
(66) El-Sayed, A. M. *The Pherobase: Database of Pheromones and Semiochemicals*, http://www.pherobase.com.
(67) Humpf, H. U.; Schreier, P. Bound aroma compounds from the fruit and the leaves of blackberry (*Rubus laciniata* L.). *J. Agric. Food Chem.* **1991**, *39*, 1830−1832.