JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

The Combined Effects of Storage Temperature and Packaging Type on the Sensory and Chemical Properties of Chardonnay

Helene Hopfer,* 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: Californian Chardonnay was stored in five different wine-packaging configurations at three different temperatures for a period of 3 months to study the combined packaging and temperature effects on the sensory and chemical properties of the wines. A trained descriptive panel evaluated aroma, taste, mouthfeel, and color attributes, and the sensory results were correlated to physical and chemical measurements including volatile compounds, SO_2, titratable and volatile acidity, oxygen consumption, and wine color, using partial least squares regression. In general, increased storage temperatures induced the largest changes in the wines; however, significant packaging−temperature effects were found for some attributes as well. Particularly wines stored in bag-in-boxes at 40 °C showed significant increases in oxidized and vinegar aromas and yellow color. Volatile esters also decreased in these wines, while increased levels of compounds generally associated with age- or heat-affected wine were found including 1,1,6-trimethyl-1,2-dihydronaphthalene and furfuryl ether, consistent with previously reported chemical aging reactions. In summary, storing unoaked Chardonnay in different packages significantly changes the sensory and chemical properties depending on the storage temperature. After a storage period of 3 months, bottle storage with various closures (natural cork, synthetic cork, and screw cap) changed the wine in a different way than bag-in-box storage.

KEYWORDS: *flavor, color, white wine, storage temperature, closure, bag-in-box*

INTRODUCTION

Wine, like every other beverage and food product, is subject to compositional changes over time due to aging-related reactions. The acceptability of aged products among consumers as well as their safety are highly dependent on the actual product: while for some foods aging may be desirable (e.g., aged cheese), for others, aging is less accepted and can even be detrimental to the safety of the food. Despite the appraisal of aged wine, most wines (90%) are being made for consumption within 12 months after production, and another 9% should not be aged over 5 years.[1] The accepted and safe age of a food or beverage is termed shelf life, "...the length of time a product may be stored without becoming unsuitable for use or consumption...".[2] The shelf life depends on many variables including the actual food or beverage itself, the production process, the storage conditions (storage temperature, humidity, etc.), and, of course, the packaging, which is capable of prolonging or, if not chosen carefully, also shortening the shelf life. For wine, the traditional packaging is a glass bottle with a natural cork closure. However, because of limited availability and natural variability of natural corks, cork taint-related issues and environmental implications, alternative packaging systems have made their way into wine packaging. There are cork alternatives (synthetic cork materials and screw caps) as well as bottle alternatives [plastic bottles and bag-in-box (BIB) solutions], which all influence the shelf life of the packaged wine in a different way as compared to the traditional wine packaging. The oxygen availability and management during storage were shown to be the crucial parameter determining the wine shelf life.[3−6] Different wine-packaging systems vary in their oxygen transmission rates (OTRs), a measure of how much oxygen is getting through the packaging into the packaged product. These values are not directly comparable due to differing ways of reporting; however, general trends can be found. On the one end of the packaging spectrum is a glass bottle with a screw-cap closure, with low OTRs in the range from 0.0002 to 0.09 mg/(L month), and on the other end is the BIB solution, an all-plastic bladder bag secured in a cardboard box, showing higher oxygen permeabilities in the range from 0.02 to 1 mL/(m^2 atm day) and oxygen ingress during filling.[7] For the BIB, up to 60% of the oxygen ingress was reported to happen through the tap (including the spout) rather than the plastic film of the bladder through the seams, and oxygen ingress is also influenced by mechanical stress of the bladder during transport.[3,7,8]

All of these results show that limitating oxygen ingress during storage is a crucial part in wine conservation. However, the complete exclusion of oxygen was also shown to be nonideal due to the formation of so-called reductive sensory characters (described as flinty or rubber), which developed in glass bottles with screw caps and glass ampules.[6] The same authors also showed that the screw-capped bottles and the glass ampule controls had a smaller degree of browning and higher amounts of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) after the 3 year storage period as compared to the natural and synthetic cork bottles. In a descriptive analysis (DA), the screw-cap samples were scored highest in fruit-related attributes (citrus, peach, and tropical) as compared to all other closures (natural cork and synthetic corks), while the synthetic corks showed the highest scores in oxidized, plastic, and wet wool attributes. Synthetic

Received: July 5, 2012
Revised: October 3, 2012
Accepted: October 4, 2012
Published: October 4, 2012

corks as alternatives to natural corks are made by either extrusion or injection-molding processes from polyethylene and, on the basis of the available literature, perform similarly to natural corks or slightly worse.[6,9] Depending on the manufacturer, their OTRs place them in between the natural corks and the plastic alternative packages with average rates between 0.006 and 0.0308 mL/day.[7]

Besides the changes in color from green and light yellow to more brown and dark hues, the aging of white wines is usually associated with the loss of fresh, floral, citrus, and fruit attributes and the development of toast, biscuit, honey, toffee, dried fruit, nutty, or kerosene and smoke characters.[6,10,11] Several studies linked these sensory changes to changes in the volatile profile of the wine and attributed the loss of the fresh fruity characters to concentration changes in various fermentation-derived esters via chemical hydrolysis reactions (fatty acid ethyl esters and acetates).[12−17] Various studies found that the acetates such as isoamyl acetate tended to decrease over storage time, while the ethyl esters either decreased or increased in their concentrations, depending on their postfermentation levels, via chemical hydrolysis and esterification.[12−17] The sensory attributes connected to aging were described as tobacco, rubber, and kerosene/diesel and seem to be linked to the formation of TDN, various aldehydes, higher alcohols, dimethyl sulfide, and diethyl succinate.[6,11,14,16−18]

A major influencing parameter for any chemical reaction is temperature, a fact that is expressed in the Arrhenius equation. This equation states that an increase in temperature increases the reaction speed exponentially. Thus, at higher temperatures, an exponential increase in the oxidation reactions in wine is expected, leading to a faster decrease of the fruit-related compounds and a faster increase in aging associated volatiles as shown by refs 11−13, 15−17, and 19−21. In a study that simulated common shipping practices for wines, Robinson et al.[20] showed that a constant 40 °C storage for 3 weeks changed the sensory profiles of four different white wine varieties to a larger extent than a diurnal temperature cycle between 20 and 40 °C or a constant 20 °C storage.

Additionally, different wine-packaging materials were shown to affect the sensory and chemical properties of wine.[3−5] Comparing Apulian white wine packaged in glass bottles with screw caps to polyethylene terephthtale (PET) bottles, Mentana et al.[4] showed that after the 7 months storage period (at 15−18 °C), the PET bottle was significantly different from the glass control in total and free SO_2 content (lower), anthocyanin content (lower), degree of browning (higher), and sensory quality (lower), with significant changes in the volatile fraction due to the loss of phenylethanol, hexanoic, octanoic, and decanoic acid, ethyl-2-hydroxy propanoate, and ethyl hydrogen succinate. The storage effects of BIBs on white Bordeaux wine properties were studied by Ghidossi et al.[5] These authors investigated 3 L BIB and observed significantly higher OTRs over the 18 months storage period as compared to the glass bottle. As a result, they found significant increases in the concentrations of the known oxidation/aging volatiles phenyacetaldehyde, methional and sotolon, as well as sensorially noticeable and significant browning, formation of oxidation characters, and loss of Sauvignon Blanc character.

The effect of storage temperature for Chenin Blanc and Chardonnay packaged in 4 L BIB on various enological parameters (browning, free and total SO_2, total phenols, and total aldehydes) was studied by Fu et al.,[3] who found that, similar to glass bottles, higher temperatures (45 °C vs 22 and 35 °C) lead to a faster decrease in total phenols, free and total SO_2, a more rapid browning, and the formation of aldehydes.

All of these studies showed separately the effect of temperature and packaging configuration on the chemical and sensory properties of white wines. In the current study, the combined effects of storage temperature and packaging type were explored. Five different packaging configurations [glass bottles with natural corks, synthetic extrusion corks, screw caps, BIB filled under normal oxygen concentrations, and BIB filled under reduced oxygen concentrations using modified atmosphere packaging (MAP) technology] were stored at three different constant temperatures (10, 20, and 40 °C) for 3 months, to study the effects on the chemical and sensory profiles of unoaked Californian Chardonnay. These three temperatures have been chosen to reflect typical wine storage temperatures, including extremes experienced during shipping or transport.[21] Even with this rather short storage period of 3 months, the observed changes in the sensory and chemical properties were statistically significant and provided the possibility to study the sensory and chemical changes due to oxidation of white wine in a short time.

MATERIALS AND METHODS

Experimental Design. Fifteen treatments were analyzed using five different wine-packaging configurations and three different storage temperatures. Three different bottle closures (natural cork, synthetic cork, and screw cap) and two BIB configurations (with and without MAP) were chosen. Each of these five packaging configurations was stored at three temperatures (10, 20, and 40 °C) for 3 months in the dark (Table 1). During the storage period, dissolved and headspace (HS) oxygen levels were monitored using noninvasive oxygen sensors (NomaSense, Nomacorc LLC, Zebulon, NC). Two bottles for each bottle treatment and one BIB for each BIB treatment were equipped with the oxygen sensors as described below. All of the wine filling and bottling was realized within 2 days in April, 2011, with the BIB, keg filling, and transport to UC Davis on the first day and filling of the bottle treatments the following day. Special care was given to avoid oxygen pick-up, temperature changes, and heating of the wine during the transport period (transport of well-cooled kegs in the evening).

Wine. Unoaked Chardonnay (vintage 2010) from the Monterey County American Viticultural Area (AVA) in California was used in the study. The wine was fined with bentonite at an average rate of 0.44 kg per 1000 L. Analyses of the ethanol concentration (13.6 v %), titratable acidity (TA) (6.1 g/L), volatile acidity (VA) (0.26 g/L), reducing sugars (5.0 g/L), free and total SO_2 (56 and 120 mg/L), and pH (3.40) were performed prior to the experiment by the winery that donated the wine and after the storage period using methods as outlined below.

Bottling and Filling of Samples. The wine for the bottle treatments was transported from Madera, CA, to the UC Davis winery in a stainless steel drum (227 L) at about 10 °C and was bottled the day after its arrival. Prior to bottling, the wine was sterilfiltered with a 0.45 μm membrane filter (Pall, Port Washington, NY) and subsequently bottled using a six-position bottling line (Costral Fiamat 2000, Riquewihr, France). All wine movements were facilitated with high purity nitrogen, and the HS in the filler bowl and in the bottles was controlled by sparging with nitrogen to avoid oxygen pick-up. Oxygen levels in the bottles were regularly checked using the oxygen sensors as described below. All closures were visually inspected for mechanical defects. Bottles with a cork closure were filled first, followed by the screw cap bottles. For each of the nine bottle treatments (three closures × three temperatures), one case (12 bottles) was filled. During the temperature treatments, bottles were stored upright. Filled bottles were kept at 10 °C for 3 days before they were transferred into their respective temperature storage units.

The same wine used for the bottle treatments was used for the BIB treatments. All BIB samples were filled in an industrial facility in

Table 1. Sample Description (Sample Codes Together with Packaging and Temperature Configuration) and Basic Chemical and Physical Color Measurements Including TA in TAE, VA in AAE, pH, Ethanol Content (EtOH), Free and Total SO_2, CIELab Lightness (L^*), Greenness (a^*), and Yellowness (b^*), and Absorbance at 420 nm (abs420) Together with the Obtained AUC Values for the HS Oxygen, DO, and TO for the 3 Months Storage Period[a]

	BIB filled at normal O_2 atm[b]			BIB filled at reduced O_2 atm[b]			bottle with natural cork[b]			bottle with screw cap[b]			bottle with synthetic cork[b]			
	10 °C	20 °C	40 °C	10 °C	20 °C	40 °C	10 °C	20 °C	40 °C	10 °C	20 °C	40 °C	10 °C	20 °C	40 °C	
code	bib10	bib20	bib40	map10	map20	map40	naco10	naco20	naco40	screw10	screw20	screw40	syco10	syco20	syco40	HSD
TA (g/L)	6.0 a	6.0 ab	5.9 d	6.0 a	6.0 abc	5.9 d	6.0 ab	6.0 abc	5.8 e	6.0 abc	6.0 c	5.8 ef	6.0 ab	6.0 bc	5.8 f	0.04
VA (g/L)	0.37 ab	0.36 ab	0.35 ab	0.38 a	0.38 a	0.36 ab	0.38 a	0.38 a	0.35 ab	0.38 ab	0.39 a	0.35 ab	0.36 ab	0.35 ab	0.31 b	0.07
pH (−)	3.53	3.56	3.53	3.53	3.6	3.61	3.54	3.54	3.56	3.53	3.52	3.53	3.53	3.55	4.19	0.9
EtOH (v %)	13.45 c	13.49 a	13.16 i	13.46 bc	13.48 ab	13.24 h	13.41 fg	13.42 efg	13.40 g	13.43 cdef	13.45 cd	13.44 cde	13.42 def	13.44 cde	13.43 cdef	0.025
free SO_2 (mg/L)[c]	35 bcde	29 cde	<10 f	38 abcd	29 cde	<10 f	40 abc	25 e	29 cde	49 a	44 ab	39 abc	40 abc	38 abcd	26 de	12.5
total SO_2 (mg/L)[c]	88 abcd	82 d	<10 f	93 abcd	86 bcd	21 e	100 ab	95 abcd	90 abcd	96 abc	101 a	99 ab	98 ab	93 abcd	83 cd	13.7
L^* (−)	65.44 de	65.72 c	64.11 f	66.07 a	65.98 ab	63.07 g	65.66 cd	65.95 ab	65.76 bc	65.80 bc	65.88 abc	65.83 bc	65.68 c	65.77 bc	65.35 e	0.226
a^* (−)	−2.11 a	−2.12 a	−2.63 e	−2.23 bc	−2.24 bc	−2.43 d	−2.15 a	−2.28 c	−2.67 e	−2.26 bc	−2.24 bc	−2.76 f	−2.22 b	−2.23 bc	−2.77 f	0.060
b^* (−)	7.17 hi	7.31 f	13.62 b	7.13 i	7.31 f	16.50 a	7.13 i	7.28 fg	8.42 e	7.21 gh	6.80 j	8.53 d	7.14 hi	7.34 f	9.69 c	0.077
abs420 (a.u.)	0.085 gh	0.089 f	0.184 b	0.084 gh	0.087 fg	0.217 a	0.081 i	0.083 hi	0.103 e	0.081 ij	0.078 j	0.107 d	0.086 fg	0.086 gh	0.128 c	0.003
AUC_HS (mg/L d)	37.4	22.9	11.2	15.4	10.9	8.9	28.1	17.2	10.8	16	7	6	28.5	22.2	13.4	
AUC_DO (ppm/d)	205.9	99.5	36.3	85.6	46.4	29.7	208	38.3	23.8	75.3	21.8	18.4	210.4	49.7	26.3	
AUC_TO (ppm/d)	243.3	122.5	47.5	101	57.3	38.6	236	55.5	34.5	91.3	28.8	24.4	238.9	71.9	39.7	

[a]Analyses are described in the Materials & Methods section. All analyses were carried out in triplicates and reported values are means together with Tukey's honestly significant differences (HSD). Rows that share the same lowercase letter are not significantly different from each other ($P \leq 0.05$). [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 caps 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 quantification (LOQ), 10 mg/L.

dx.doi.org/10.1021/jf302910f | J. Agric. Food Chem. 2012, 60, 10743−10754

Madera, CA, which used MAP conditions to fill the bags with lower oxygen concentrations (down to 1−2% oxygen). Two BIB packaging treatments were realized by filling samples with the MAP conditions switched on, and without the MAP conditions, to study the impact of reduced oxygen during the filling on the wine properties. MAP samples were filled first, and then, the MAP system was switched off, and after an equilibration period of about an hour, the other samples were filled. For both BIB treatments, three BIBs equipped with oxygen sensors were marked and inserted to the filling process spread over the sampling period. For each of the six BIB treatments (two BIB oxygen concentrations during filling × three temperatures), eight BIBs (3 L volume each) were filled. Filled samples were kept at 10 °C for 4 days before they were transferred into their respective temperature storage units.

Storage Conditions. The 10 °C storage was carried out in a temperature-controlled chill room with a mean temperature of 10.0 ± 1.0 °C. All samples were placed together in a corner of the room. The 20 °C storage was carried out in a temperature-controlled room that was used for sensory evaluations, where the samples were locked away in cabinets. The average temperature was 20.8 ± 1.3 °C, monitored by four temperature loggers (Tinytag Transit 2 TG4080, Gemini Data Loggers, West Sussex, United Kingdom). For the 40 °C storage, four 200 L temperature-controlled tanks (designed, fabricated, and donated by a team of research engineers led by T. J. Rodgers, Cypress Semiconductor, San Jose, CA), equipped with temperature sensors (HOBO U12 4-Channel External Data Logger with four TMC-HD temperature probes), were used. The average temperature was 43.5 ± 1.0 °C.

Oxygen Measurements. Two bottles of each treatment were equipped with two noninvasive oxygen sensor spots, each which measured the HS and the dissolved oxygen (DO) throughout the storage period (5 mm sensor spots PSt3, NomaSense, Nomacorc LLC). The HS sensor dot was placed in the lower part of the bottleneck and was above the liquid, while the DO sensor dot was glued in the middle part of the bottle body, in contact with the wine during all time. For the BIB treatments, one BIB was equipped with one oxygen sensor spot, glued near the spout, and DO levels were measured using the same one sensor after the initial HS reading by inverting the BIB and after an equilibration period of 5 min. Oxygen levels were checked throughout the storage period 19 times, with daily measurements in the first 2 weeks (5 times per week, Monday through Friday), three times per week for week 3 (Monday, Wednesday, and Friday), and once a week thereafter (Mondays). Measurements were temperature compensated using the attached temperature probe and were taken after equilibrium was reached. The limits of detection were 0.31 hPa for HS values and 15 ppb (=0.015 ppm) for DO according to the manufacturer's specifications. HS values were measured in hPa and % oxygen, and DO was measured in ppm. DO levels were corrected for the different volumes of the BIB and bottle treatments. Total packaged oxygen (TO) in ppm was calculated from the HS and the DO values as the sum of the two, after the HS values were converted into ppm. For the bottle treatments, a constant HS volume of 4.71 mL was used. For the BIB treatments, the HS volume was measured using the BIB cone meter.[22] For the calculation of the area under the curve (AUC) values, bottle measurements were averaged over the duplicates and reported as ppm per day (ppm/day).

Sensory Analysis. A generic DA for aroma, taste, mouthfeel, and color attributes was performed in triplicate as described in detail in ref 23. Twelve panelists (four males and eight females; aged 21−68 years; eight with previous DA experience) were recruited from the students, faculty, staff, and retirees of the Departments of Viticulture & Enology and Food Science & Technology based on their availability and willingness to participate and took part in six 1 h training sessions over the period of 2 weeks. The training was followed by nine 30 min evaluation sessions over a period of 3 weeks. The Institutional Review Board of UC Davis approved the study, all participants gave informed oral consent, and no monetary compensation was provided (protocol number 201018548-1).

For the aroma, taste, and mouthfeel attributes, the panelists were presented with subsets of the wines during the training sessions and asked to generate, combine, and obtain consensus on the reference standards (Table 2). Each wine treatment was shown blindly at least twice during the training sessions to the panelists. Wines were evaluated for aroma, taste, and mouthfeel attributes in individual tasting booths under white light and in pear-shaped black ISO glasses[24] labeled with three digit random numbers. Panelists evaluated six wines per session and were asked to expectorate all samples. Filtered water (Arrowhead, Nestle Waters America, Stamford, CT) and unsalted crackers (Nabisco unsalted top premium saltine crackers, Kraft Foods, Northfield, IL) were provided for palate cleansing. A 1 min break between each wine and a 3 min break between the third and the fourth wine were included to decrease palate fatigue. Samples were presented in an incomplete William Latin Square design provided by FIZZ (Biosystemes, Couternon, France), which was also used for collecting the aroma, taste, and mouthfeel scores on an end point labeled and anchored line scale.

For the color DA, paint color chips from a local hardware store (ACE Hardware, Davis, CA) were used as references and given to the panelists during the training sessions, where they were asked to choose up to two different colors for each wine (Table 2). All panelists were screened for color blindness in the first training session using pseudoisochromatic color testing plates (American Optical Corporation, Ontario, Canada), and all of them were considered to have normal color vision as they could identify at least six out of seven testing plates correctly. The test was used for screening purposes only and was designed to detect red−green defects. The panelists evaluated the color of the wine samples in the booths, where the reference paint chips and an evaluation sheet were presented together with six wines in pear-shaped transparent ISO glasses,[24] which were labeled with three digit random number, differing from the aroma, taste, and mouthfeel DA numbers. All color evaluations took place in separate individual booths, different from the aroma, taste, and mouthfeel DA, under defined illumination conditions.[23] Panelists were given the choice of evaluating color before or after the aroma, taste, and mouthfeel DA. The evaluation table had an off-white background color and two vertically mounted halogen lamps (1.4 m distant from the table surface, 30 cm distant from each other) with a color temperature of 3000 K and were used at maximum luminous intensity of the lamp of 1580 cd (MR16 Superline Reflekto, Ushiro America Inc., Cypress, CA). The spectral distribution of the lamps resembled a CIE standard illuminant A with more yellow and red wavelengths. During the training sessions, the panelists agreed by consensus to evaluate the color close to the rim of the glass at an angle of 45° with the base back touching the table surface, so that the panelists' eyes were about 35−40 cm distant from the glass. Each paint reference chip chosen by the panelists in the wine evaluations was measured in triplicate with a chromameter (Konica Minolta Sensing Americas, Inc., Ramsey, NJ) to obtain the CIELab color values, which were then used in all further data analyses.

Instrumental Color Measurement. For each wine, the CIELab color space values[25,26] were measured in triplicate with a chromameter, equipped with a 10 mm wide cell [CR-400 with a pulsed xenon lamp as light source and a 2° Observer, which closely matches the CIE 1931 Standard Observer and a C* illuminant (Konica Minolta Sensing Americas, Inc.)]. The surrounding was the same as in the color DA sessions. Prior to the measurements, the chromameter was calibrated on a white calibration plate. Demineralized water was used for blank measurements. In addition, the absorbance at 420 nm was measured for all wine samples in triplicate using a UV/vis spectrophotometer (Thermo Scientific BioMate 3S, West Palm Beach, FL) in semicuvettes with a path length of 1 cm.[27,28] The absorbance at 420 nm is a typical wavelength to detect browning in white wines.[28] Colors were expressed as CIELab values L^* (lightness ranging from black for 0 and 100 for white), a^* (from $+a^*$ for red to $-a^*$ for green color), and b^* (from $+b^*$ for yellow to $-b^*$ for blue color).

Basic Chemical Analyses. Changes in the wine composition resulting from the different storage and packaging conditions were determined at the end of the storage period by measuring TA and VA, pH, ethanol, and SO_2 (free and total) in triplicate. TA was expressed as tartaric acid equivalents (TAE), and pH and free and total SO_2 were determined as described by refs 27 and 28. VA as acetic acid

Table 2. Reference Standards for the 18 Aroma, Taste, and Mouthfeel Attributes and the Color Codes Used in the DA, Together with the Used Anchor Words[a]

aromas[b]		reference standard	anchors
fruit	tropical fruit	20 mL of guava nectar (Kern's) + 15 mL of peeled whole lychee syrup (Dynasty) in 40 mL	low−high
	apple/pear	10 g of cut fresh green apple + 12 g of cut fresh pear in 20 mL	
	melon	14 g of cut cantaloupe melon without rind in 10 mL	
	cherry	10 halved frozen cherries (Dole dark sweet cherries) in 20 mL	
peach	12.8 g of fresh cut peaches in 10 mL		low−high
citrus	0.5 g of cut lime peel + 0.3 g of cut lemon peel + 0.5 g of cut grapefruit peel in 20 mL		low−high
green	grassy	2.4 g of fresh cut grass in 10 mL	low−high
	canned veggie	1 tsp of green chiles brine (La Victoria) + 2 tsp of each canned pea brine (Del Monte fresh cut sweet peas) + canned green bean brine (Best Yet not salted green beans) in 20 mL	
	unripe fruit	verbal description: the green, unripe smell of unripe peaches or pears	
waxy	crayon tips (Crayola, Easton, PA); no wine		low−high
vinegar	5 mL of Barengo Vineyard's Balsamic Vinegar di Modena PGI in 40 mL		low−high
alcoholic	30 mL of Sobieski Vodka 40% in 30 mL		low−high
oxidized	Sherry	10 mL of Domecq Manzanilla Light Sherry in 30 mL	low−high
	dried fruit 1	1 dried halved apricot + 1/2 sliced prune + 4 raisins + 1/2 dried sliced Mission Fig (all SunMaid) in 30 mL	
	dried fruit 2	1 sliced prune + 1 dried sliced Mission Fig + 5 raisins (all SunMaid) in 30 mL	
musty	4 mL of organic acid stock solution (sodium tartrate, sodium L-lactate, sodium malate, sodium succinate, and sodium citrate, 1 g anion/L each in organic acid buffer) in 20 mL		low−high
honey	10.2 g of mashed ripe banana + 4.2 g of honey + 0.1 mL of vanilla extract (Kirkland) in 20 mL		low−high
oak/spicy	0.3 g of EvOak American Oak High toast small chips (Oak Solutions) + 2 crushed black peppercorns (McCormick) in 30 mL		low−high
sulfur	rotten egg	1 overcooked hard boiled egg, cut in half	low−high
	skunk	20 mL of light-stuck beer (Corona Extra stored in the sun for 3 days)	
	matchstick	verbal description: the pungent, burnt smell of freshly lit matchstick	

taste and mouthfeel[c]	reference standard	anchors
astringent	high, 312 mg/L alum (McCormick); low, pure water	low−high
sour	high, 2 g/L tartaric acid (Sigma-Aldrich, St. Louis, MO); low, 0.5 g/L tartaric acid	low−high
sweet	high, 7 g/L sucrose; low, pure water	low−high
bitter	high, 1 g/L caffeine (Sigma-Aldrich); medium, 0.5 g/L caffeine; low, pure water	low−high
hot	10 v % 96% ethanol (GoldShield)	low−high
fullness	thin, 0.5 g/L carboxymethyl cellulose (Sigma-Aldrich); thick: 1.5 g/L carboxymethyl cellulose	thin−thick

colors[d]	
Benjamin Moore (Montvale, NJ)	2018−2027, 2149, 2151, 1211−1214, 1288−1293, 1330−1333, 1337−1338, 1343, 1378, 1386−1389
ACE paint (Oak Brook, IL)	A24−A26, C24−C30

[a]For some references, more than one standard was available, but panelists rated only the combined attribute. [b]All aroma standards were prepared in base wine (Franzia Vintner's Select Chardonnay) unless otherwise noted. [c]All taste and mouthfeel standards were prepared in Arrowhead Mountain spring water. [d]Numbers refer to color card codes.

equivalents (AAE) was determined using an enzymatic kit (Unitech Scientific Flex-Reagent, Hawaiian Gardens, CA). Ethanol levels were measured with an Alcolyzer Wine M/ME (Anton Paar, Graz, Austria).

HS Solid-Phase Microextraction Gas Chromatography−Mass Spectrometry (HS-SPME-GC-MS). An Agilent 7890 GC was coupled to an Agilent 5975C inert XL EI/CI MS (Santa Clara, CA), equipped with a CTC CombiPal autosampler (Zwingen, Switzerland). For compound separation, a DB-WAX capillary column (30 m × 0.25 mm × 0.25 μm; Agilent) was operated in constant flow mode (0.8 mL/min) using a splitless mode after 1 min. The oven program started at 40 °C and was held there for 1 min, and then, the temperature was ramped at 5 °C/min to 250 °C with a final hold of 5 min. The injector was held at 240 °C and was equipped with a 0.75 mm inner diameter inlet liner (Supelco, Bellefonte, PA). The MS source and quadrupole temperatures were set at 230 and 150 °C, respectively. MS spectra were obtained in electron ionization mode scanning from 50 to 400 m/z with a solvent delay of 4.5 min. For analysis, 5 mL of wine sample together with 2 g of NaCl (Fisher Scientific, Pittsburgh, PA) and 10 μL of internal standard (IS) solution [50 ppm 2-octanol (97+%, Sigma-Aldrich, St. Louis, MO) in ethanol (Goldshield 200 proof, Hayward, CA)] were added to a 20 mL brown HS vial (Agilent), closed with a magnetic crimp cap [polytetrafluoroethylene (PTFE)-silicone septum, Sigma-Aldrich], and extracted for 15 min at 40 °C after an incubation time of 5 min using a 2 cm divinylbenzene/carboxen/polydimethylsiloxane (DVB/Car/PDMS) 50/30 μm SPME fiber (Supelco). Retention indices (RIs) were determined by analyzing an alkane standard mixture (5 μL C8 to C32 n-alkanes in n-hexane (100−200 ppm), Sigma-Aldrich) under the described conditions with a 30 min of extraction time instead of 15 min. Volatile compounds were identified by matching mass spectra from the NIST 08 Library (Scientific Instrument Services, Inc., Ringoes, NJ) and RIs with reported literature values and authentic standards when available. Compound concentrations were reported semiquantitatively as IS equivalents in μg/L to compare relative concentration changes among the studied samples only.

Statistical Analyses. Results from the DA (aroma, taste, and mouthfeel attributes rated on a line scale) were analyzed using multivariate analysis of variance (MANOVA) on the product effect and univariate analysis of variance (ANOVA) for the fixed effects judge (J), packaging (P), temperature (T), replicate (R), and the packaging−temperature interaction (P:T), both at an α level of 5% for all analyses. This procedure protected against type I errors.[23] Significant attributes from the ANOVAs were used in a subsequent canonical variate analysis (CVA) to compare the products graphically. Because of the nature of the CVA using raw data, the ability to plot confidence intervals (CI) around the product means provides a graphical representation of significance testing [i.e., spheres that do not overlap are statistically different ($P \leq 0.05$)].

For all other analyses (color DA, instrumental color measurements, volatile profile, and basic chemical analyses), obtained data were first analyzed with MANOVA and ANOVA, followed by principal component

analysis (PCA) on averaged data. For the data analysis of the color DA, the reference paint chips were converted into their respective CIELab color values. A PCA using the correlation matrix to account for scaling differences was used to compare the products across the instrumental and chemical measurements.

For the oxygen data (HS oxygen and DO changes over the storage period in all treatments) a repeated measure ANOVA for significant differences between the treatments was performed using the main effects packaging (P), temperature (T), and storage time (t) and the interaction terms P:T, t:P, t:T, and t:T:P ($P \leq 0.05$). In addition, the AUC was determined for all HS, DO, and TO data over the whole storage period. These values were used as measures for the oxygen consumption, assuming that the faster the oxygen is consumed the smaller the AUC values get.

Last, partial least squares regression (PLS), a combination of multiple regression and PCA,[29] was employed to correlate and predict the sensory variables by the chemical and physical measurements.[29−31] All physical and chemical analyses (instrumental CIELab, absorbance at 420 nm, volatiles, and basic chemical wine parameters) and the oxygen AUC values (HS, DO, and TO) were included to predict all sensory attributes (aroma, taste, mouthfeel, and color). SAS (SAS Institute Inc., Cary, NC) was used for the repeated measure ANOVA, and *R* with the SensoMineR, FactoMineR, and pls packages was used for all other analyses.[32−35]

RESULTS AND DISCUSSION

Sensory Analysis. Using DA, sensory differences among the wines in terms of aroma, taste, mouthfeel, and color attributes, caused by the different storage temperatures and packaging types, were found. Significant differences ($P \leq 0.05$) among the samples were found in the multivariate analysis of variance (MANOVA) on the wine effect. In the four-way fixed effect, univariate analysis of variance (ANOVA) for the 18 aroma, taste, and mouthfeel and the three color attributes using the effects of judge (J), packaging (P), temperature (T), replicate (R), as well as the packaging−temperature interaction (P:T), nine of the 18 flavor and all three color attributes showed a significant temperature effect (fruit, peach, citrus, vinegar, oxidized, musty, sulfur, bitter, hot, DA_*L**, DA_*a**, and DA_*b**), four showed a significant packaging effect (oxidized, hot, DA_*L**, and DA_*b**), and one attribute was significant for the P:T interaction (oxidized) (all $P \leq 0.05$). A table of the means together with the Tukey's honestly significant differences (HSD) is shown in Table 3a,b: At 40 °C, the perception of all significant sensory attributes was different from the attributes in wines stored at the lower temperatures (Table 3a). As expected from earlier studies,[19,20] all fruit-related attributes (fruit, peach, and citrus) decreased with increasing storage temperature, while the vinegar, oxidized, musty, sulfur, and bitter descriptors increased with increasing storage temperature. The hot mouthfeel attribute decreased in samples stored at higher temperatures, suggesting a loss of ethanol in the wine; ethanol has previously been shown to elucidate a warming sensation.[36−38] Furthermore, the attributes hot and oxidized were different for the different packaging types (Table 3b). The hot mouthfeel attribute also showed a significant packaging effect with significantly lower scores in the BIB treatments (bib and map). Possibly, the ethanol migrated through the BIB during the storage period or took part in chemical reactions during the storage period. Ethanol analysis after the storage period for all samples revealed significant differences for both the temperature and the packaging variables (Table 1). While the bottle closure treatments (syco, naco, and screw) did not show any significant differences among the three storage temperatures, both of the BIB treatments (bib40 and map40) had significantly lower ethanol concentrations after being stored at 40 °C. For the BIB samples, even storage at 20 °C (bib20) resulted in significantly lower alcohol concentrations as compared to the 10 °C treatment (bib10). Combining both the sensory and the chemical analyses, these results revealed a noticeable change in the ethanol content when wine was stored in different packages and/or at different temperatures.

Table 3. Overall Mean Values and Tukey's HSD Levels for the Significant Flavor and Color DA Attributes ($\Pi \leq 5$) Separated for the Temperature Effect (a), Packaging Effect for Each Packaging Type (b), and Separated between BIB (Map and Bib) and Bottle (Naco, Syco, and Screw) Treatments (c)[a]

	temperature			
(a)	10 °C	20 °C	40 °C	HSD
fruit	2.9 a	2.9 a	2.1 b	0.5
peach	2.1 ab	2.4 a	1.8 b	0.5
citrus	2.0 a	1.8 a	1.2 b	0.4
vinegar	1.8 a	2.3 ab	2.4 b	0.5
oxidized	1.8 a	1.8 a	4.0 b	0.5
musty	1.2 a	1.3 a	1.8 b	0.3
sulfur	1.5 a	1.5 a	2.3 b	0.4
bitter	1.7 a	1.8 a	2.2 b	0.3
hot	3.3 a	3.5 a	2.8 b	0.4
DA_L*	93.8 a	93.8 a	91.7 b	0.5
DA_a*	−5.0 a	−5.4 b	−5.9 c	0.4
DA_b*	23.0 a	24.0 a	34.7 b	1.8

	packaging					
(b)	bib	map	naco	syco	screw	HSD
oxidized	3.3 a	3.1 a	1.9 b	2.1 b	2.1 b	0.68
hot	2.8 a	3.3 ab	3.1 ab	3.5 b	3.0 ab	0.58
DA_*L**	92.4 a	92.4 a	93.7 b	93.7 b	93.6 b	0.73
DA_*b**	29.8 a	31.4 a	24.9 b	24.5 b	25.1 b	2.73

(c)	BIB	bottles	HSD
oxidized	3.2 a	2.03 b	0.68
hot	3.05 a	3.20 a	0.58
DA_*L**	92.4 a	93.67 b	0.73
DA_*b**	30.6 a	24.83 b	2.73

[a]Rows sharing the same letter are not significantly different.

All three CIELab color space values were also significantly different for the samples stored at 40 °C ($P \leq 0.05$). The lightness DA_*L** decreased for the two BIB samples (bib and map) with increasing storage temperatures, indicating a browning of the sample. This was not found at all for the bottle treatments, where no significant effect due to the storage temperature was observed for the DA_*L** value. On the other hand, an increase in storage temperature resulted in a decrease in the measured DA_*a** values (i.e., reduced green color) for all packaging types. Yellowness increased (i.e., increase in DA_*b**) significantly for the wine stored in the 40 °C BIB treatments (bib40 and map40); for all bottle treatments (naco40, syco40, and screw40), yellowness was also higher following storage at 40 °C, but the effect was not statistically significant ($P \leq 0.05$). Similar results for Spanish white wines were reported by ref 39. With increasing storage time, Zalema white wine changed its color from pale yellow (i.e., high in *L**, low in *a**, and low in *b**) to yellow brown (lower *L**, higher *a**, and higher *b**).

Comparing both BIB treatments (map and bib) to all three bottle treatments (naco, syco, and screw) as shown in Table 3c, significant differences across all storage temperatures were found between the two packaging types for the sensory

attributes oxidized, DA_L*, and DA_b* but not for the hot mouthfeel.

A graphical representation of the sample space obtained from a canonical variate analysis (CVA) on the aroma, taste, and mouthfeel attributes is shown in Figure 1. Within the first two

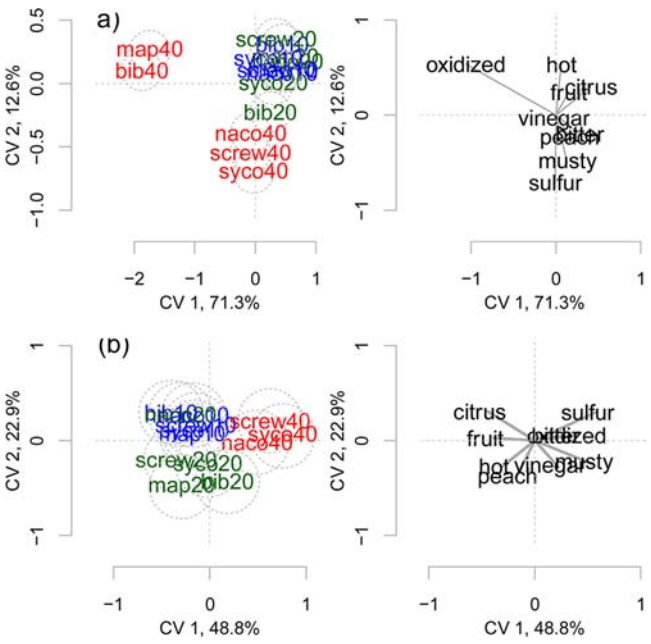

Figure 1. Graphical sample and attribute space representation using the significant aroma, taste, and mouthfeel attributes from the DA using a canonical variate analysis (CVA). (a) CVA with all samples and (b) CVA without the 40 °C BIB treatments (bib40 and map40). Samples are colored according to their storage temperature (blue, 10 °C; green, 20 °C; and red, 40 °C) and coded as explained in Table 1. The 95% CI according to Chatfield and Collins[40] is indicated by the circles around the sample mean positions.

dimensions, nearly 84% of the total variance ratio could be explained with about 71% explained in the first canonical variate CV 1 (Figure 1a). Most 40 °C treatments were significantly different ($P \leq 0.05$) from the 10 and 20 °C treatments, with the exception of naco40, which was not significantly different from bib20, indicated by the overlap of the 95% CI circles around the samples means.[40] The storage temperature was the major driving factor along CV 1 differentiating between the 10 and the 20 °C samples on the right-hand side of the plot and the BIB 40 °C samples (bib40 and map40) on the left-hand side. A clear separation for the attributes was found for the oxidized aroma, exclusively explaining the 40 °C BIB treatments, the musty and sulfur descriptors, being highly correlated to the 40 °C bottle treatments, and the remaining attributes (fruit, citrus, hot, bitter, and peach) explaining the 10 and 20 °C samples. One significant attribute (vinegar) showed a low loading on both dimensions and was located around the center.

Because of the large differences between the 40 °C BIB samples (bib40 and map40) and the rest of the treatments, the CVA was rerun without the former two samples, and the plots shown in Figure 1b were obtained: A clearer separation between the 10 and the 20 °C treatments was found, with the 20 °C treatments being located in the bottom left corner, and the 10 °C samples being located in the top left corner with the exception of the wine with the natural cork closure stored at 20 °C (naco20), which remained clustered with the wines stored at 10 °C. While the wines in the former group (20 °C storage) showed a high positive correlation to the attributes hot, peach, vinegar, and musty, the wines in the latter group (10 °C storage) were described by fruit and citrus aromas and bitter taste. The three 40 °C bottle samples are located on the positive CV 1 axis and showed a high correlation to musty and sulfur aroma attributes. The oxidized attribute was only minimally loaded in this plot, indicating the importance of this attribute solely for the 40 °C BIB samples (bib40 and map40).

From the sensory color evaluations, the PCA product and variable plots in Figure 2a were obtained. Similarly to the flavor DA, the dissimilarity between the two 40 °C BIB treatments (bib40 and map40) and the rest of the samples is driving the separation along the first principal component PC 1 (explained variance of 99.6%). This differentiation can be explained by two of the three color space values (lightness DA_L* and yellowness DA_b*). While the two 40 °C BIB samples were more yellow and darker in color (high DA_b* and low DA_L* values), the wines were stored in bottles at 40 °C (for all three closure types), and all of the 20 °C treatments positively correlated to DA_L*, indicating a lighter color and the absence of yellowness (low DA_b*). The remaining samples (all 10 °C treatments) located in the top right corner were positively correlated to a slight green color (−DA_a* value).

Chemical and Physical Measurements. The changes in the wines due to the different temperature and packaging treatments were studied using various chemical and physical measurements as described in the Materials and Methods. Univariate ANOVAs for each instrumental color variable (L*, a*, b*, and abs420) using packaging, temperature, and the interaction as fixed effects revealed significant differences among the samples ($P \leq 0.05$), after the multivariate analysis showed a significant product effect ($P \leq 0.05$). Similar to the sensory color DA, the lightness L* and the greenness a* significantly decreased with increasing temperature, while the yellowness b* and the absorbance abs420 increased significantly with increasing storage temperature. Again, the wines stored at 40 °C were most different from all other treatments. For the L* and a* measurements, the means were similar for all wines stored in the bottles regardless of the closure type. Means for the b* and abs420 measurements tended to be lower for wines stored in bottles with synthetic cork as compared to natural cork and screw-cap closures; however, the differences were not statistically different ($P \leq 0.05$) (Table 1).

In Figure 2b on the left, the PCA product plot of the instrumental color measurements looked very similar to the one obtained from the color DA (Figure 2a). Samples were separated along the first principal component PC 1 between the two 40 °C BIB treatments and all other samples (accounting for 80% of the explained variance). The second dimension PC 2 explained an additional 19.5% of the total variance and separated the 40 °C bottle treatments (naco40, syco40, and screw40) from the 10 and 20 °C samples, and the latter treatments formed a group in the top left quadrant of the plot. The separation of the wines along PC 1 was due to three out of the four measured values. While the two 40 °C BIB treatments were highly positively correlated to b* (i.e., high in yellow color) and abs420, the other samples showed a high positive correlation to lightness L*. Along PC 2, the fourth variable (a*) separated the samples according to their green color. Similar results for Spanish white wines were reported by ref 39. With increasing storage time, Zalema white wine changed its

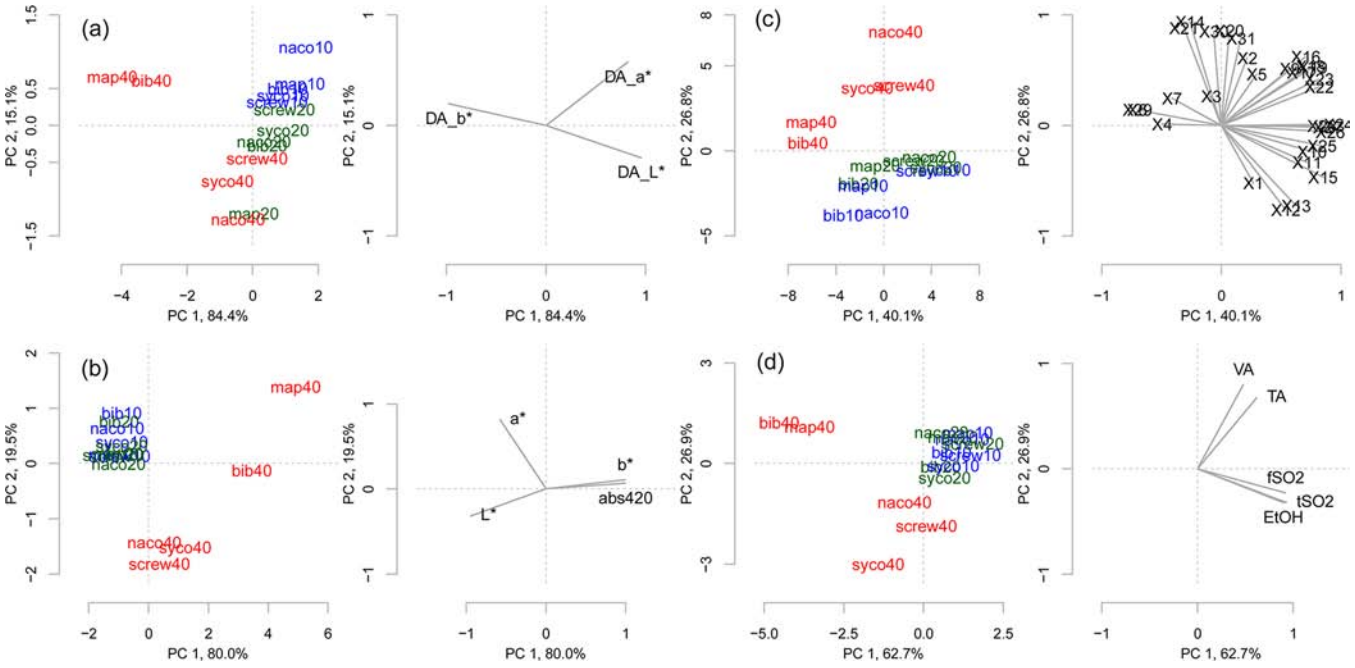

Figure 2. (a–d) PCA product and variables plots. (a) Color DA using color paint chips as reference standards and translating these references into CIELab color space values (DA_L*, DA_a*, and DA_b*), (b) instrumental color determination using the Chromameter CIELab values (L*, a*, and b*) and the absorbance at 420 nm (abs420), (c) volatiles determined by HS-SPME-GC-MS with sample and compound codes according to Tables 1 and 3, and (d) basic chemical measurements [TA, VA, free and total SO_2 (fSO_2, tSO_2), and ethanol content (EtOH)]. Samples are colored according to their storage temperature (blue, 10 °C; green, 20 °C; and red, 40 °C) and coded as explained in Table 1.

color from pale yellow (i.e., high in L*, low in a*, and low in b*) to yellow and brown (lower L*, higher a*, and higher b*).

In the volatile data analysis, all 30 identified compounds were found to be significantly different using a fixed effect ANOVA model with product and replicate effects ($P \leq 0.05$) (Table 4), after the MANOVA revealed a significant product effect ($P \leq 0.05$). A table with mean values and standard deviations can be found in Table 1 in the Supporting Information. In the PCA (Figure 2c), 67% of the variance could be explained within the first two dimensions. Along the PC 1, explaining 40% of the total variance, samples were separated based on their packaging material with the BIB treatments on the left-hand side and the bottle treatments on the right-hand side with the exception of the natural cork sample at 10 °C (naco10), which was grouped closer to the BIB samples than the bottle treatments. On PC 2, explaining an additional 27% of the total variance, the samples were separated by storage temperature with the 40 °C treatments in the top part of the product space and the 10 and 20 °C samples in the bottom part of the graph. As expected, the 10 and 20 °C bottle treatments in the bottom right quadrant showed a high positive correlation to the ethyl esters X24–X28, 2-methyl propanol (X1), the two terpenoid alcohols hotrienol and linalool (X10 and X11), and the acetates X12, X13, and X15, which are all contributing to the fresh and fruity aroma and flavor of these wines as described earlier in the literature.[11,41] The concentrations of the alcohols X3 and X7, as well as diethyl succinate (X14), the ester X21, and the furfuryl ether (X30), were reduced in these samples, thus showing a negative correlation in the product space (see also Table 1 in the Supporting Information). For the BIB samples stored at the low temperatures (10 and 20 °C), different volatile profiles were obtained. These samples were mainly characterized by low amounts (i.e., negative correlation) of various acids (X16–X20), ethyl esters (X22 and X23), alcohols (X2, X5, and X9), and the compound TDN (X31), which was previously reported to contribute to the diesel/kerosene aroma of aged Riesling and other white varieties[6,20,42] (see also Table 1 in the Supporting Information). We hypothesize that the differences in the flavor profile between the BIB and the bottle treatments resulted from either the higher oxygen present in the BIB samples during the storage period or possible flavor scalping phenomena, as various esters have been shown to be easily scalped by plastic films.[43–45] It was also shown that the presence of ethanol facilitates the scalping process even more, particularly between 5 and 15 v% ethanol.[43–45] Possibly a combination of both phenomena played a role in the changes in volatile composition. All 40 °C bottle treatments at the top of the graph are positively correlated to straight chain and (m)ethyl-branched alcohols (X2, X3, and X5), ethyl-3-methyl butanoate (X21), diethyl succinate (X14), the furfuryl ether (X30), and TDN (X31). All of these compounds were previously reported in aged wines and are likely contributing to the sensory changes.[17,20] The two 40 °C BIB treatments (bib40 and map40) showed the highest correlation to 1-butanol (X4), *n*-hexanal (X29), and 2-ethyl hexanol (X6), while the synthetic cork sample (syco40) was positioned in between the two 40 °C groups (BIB and bottles) and showed the highest correlation to 1-octanol (X7).

For the basic chemical measurements, all six measurements [TA, VA, pH, ethanol content (EtOH), and free and total SO_2 content (fSO_2 and tSO_2)] were found to be statistically significant with the exception of pH ($P \leq 0.05$), using a fixed effect model with sample and replicate effects (Table 1). For all basic chemical measurements, a decrease with increasing storage temperature was observed. TA decreased significantly for all 40 °C treatments, independent of their packaging configuration, while a significant decrease for VA was only observed for the synthetic cork stored at 40 °C (syco40). Free and total SO_2 decreased as expected with increasing storage temperature

Table 4. Identified Volatile Compounds Found in the Samples with Their Identification Features

code	compd	CAS	unique ion[a]	RT[b]	RI[b]	RI (lit)[c]	identified[d]
X1	2-methyl propanol	78-83-1	56	5.700	1097	1108	RI, MS, ref
X2	2-methyl butanol	137-32-6	56	8.195	1202	1206	RI, MS, ref
X3	3-methyl butanol	123-51-3	60	8.779	1224	1230	RI, MS, ref
X4	1-butanol	71-36-3	56	6.739	1141	1138	RI, MS, ref
X5	1-hexanol	111-27-3	56	11.837	1336	1360	RI, MS, ref
X6	2-ethyl hexanol	104-76-7	56	15.201	1468	1487	RI, MS, ref
X7	1-octanol	111-87-5	56	16.844	1545	1388	RI, MS, ref
X8	2-octanol (IS)	123-96-6	56	13.531	1391	1332	RI, MS, ref
X9	2-phenethyl alcohol	60-12-8	104	24.432	1904	1905	RI, MS, ref
X10	hotrienol	29957-43-5	82	17.99	1598	1085	RI, MS
X11	linalool	78-70-6	93	16.547	1532	1537	RI, MS, ref
X12	3-methyl butanol acetate	123-92-2	56	6.046	1112	1118	RI, MS, ref
X13	1-hexyl acetate	142-92-7	56	9.708	1260	1270	RI, MS, ref
X14	diethyl succinate	123-25-1	56	19.477	1666	1689	RI, MS, ref
X15	2-phenylethanol acetate	103-45-7	104	22.427	1806	1803	RI, MS, ref
X16	butanoic acid	107-92-6	60	18.816	1636	1644	RI, MS, ref
X17	hexanoic acid	142-62-1	60	23.152	1841	1863	RI, MS, ref
X18	octanoic acid	124-07-2	60	27.467	2040	2083	RI, MS, ref
X19	decanoic acid	334-48-5	60	31.348	2194	2296	RI, MS, ref
X20	2-hydroxypropanoic acid	50-21-5	56	11.416	1323	n.a.	MS
X21	ethyl 3-methyl butanoate	108-64-5	56	4.963	1057	1060	RI, MS, ref
X22	ethyl hexanoate	123-66-0	88	8.778	1224	1220	RI, MS, ref
X23	ethyl heptanoate	106-30-9	88	11.176	1315	894	RI, MS, ref
X24	ethyl octanoate	106-32-1	88	14.055	1413	1436	RI, MS, ref
X25	ethyl nonaoate	123-29-5	88	16.258	1519	1636	RI, MS, ref
X26	ethyl decanoate	110-38-3	56	18.822	1636	1636	RI, MS, ref
X27	ethyl 9-decenoate	67233-91-4	88	19.836	1683	1694	RI, MS, ref
X28	ethyl dodecanoate	106-33-2	88	23.169	1842	n.a.	MS
X29	1-hexanal	66-25-1	56	5.192	1069	1084	RI, MS, ref
X30	furfuryl ether	4437-22-3	82	9.966	1270	n.a.	MS
X31	TDN	30364-38-6	157	20.854	1731	n.a.	MS, ref

[a]Ion (m/z) used for quantification. [b]Determined on a DB-WAX (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Agilent, Santa Clara, CA). [c]Retention index (RI) literature (lit) values are taken from Flavornet and Pherobase unless otherwise noted;[46,47] NA annotates not available RIs. [d]Compound identification was done by matching measured RIs with literature values (RI), matching mass spectra with spectrum library (MS), and matching with authentic references (ref).

and were significantly different in all packaging configurations at 40 °C with the exception of the screw-cap samples (Table 1).

The subsequent PCA included only the five significant variables and is shown in Figure 2d, explaining nearly 90% of the total variance within the first two dimensions. As expected, the two 40 °C BIB samples (bib40 and map40) were negatively correlated to ethanol (EtOH) and free and total SO_2 (fSO_2 and tSO_2) contents and positioned in the left side of the product plot. All 10 and 20 °C treatments on the right-hand side of the product plot showed a positive correlation to the two acidity measurements (TA and VA), while the 40 °C bottle treatments in the bottom left quadrant showed a negative correlation to these two parameters, indicating lower amounts of total and volatile acidities. As previously discussed in the sensory results section, the ethanol content decreased significantly in the two BIB treatments at 40 °C (from 13.45 v% down to 13.16 v% for the bib samples, similarly for the map samples from 13.46 v% down to 13.24 v%). Possibly, the ethanol migrated through the BIB during the storage period or took part in chemical reactions during the storage period. A similar behavior was just recently described by Peyches-Bach et al.:[43] They observed an ethanol mass uptake by a food grade PE film of 3.89 kg/m^3 from a 12 v% ethanolic solution after 21 days of contact, and this might be the explanation for the observed effect in our study. Although not studied by the authors, the higher storage temperature used in our study could have possibly increased the effect, as this was only observed at the higher storage temperature and not at the lower ones.

Table 5. Cumulative Explained Variance for the Predicting Matrix X (Chemical and Physical Variables) and Each of the Predicted Variables (Sensory Attributes) for the First Three Latent Vectors (Comps) in the PLS Regression

%	1 comp	2 comps	3 comps
X	15.3	38.8	64.7
fruit	63.6	69.0	73.4
peach	60.2	61.7	79.9
citrus	52.4	59.3	61.3
vinegar	9.6	40.8	40.8
oxidized	82.6	88.4	89.2
musty	32.0	36.4	38.1
sulfur	20.6	20.6	35.1
bitter	26.8	27.8	29.4
hot	43.0	44.1	46.1
DA_L*	82.0	90.2	91.1
DA_a*	31.1	62.9	65.2
DA_b*	81.4	91.5	93.8

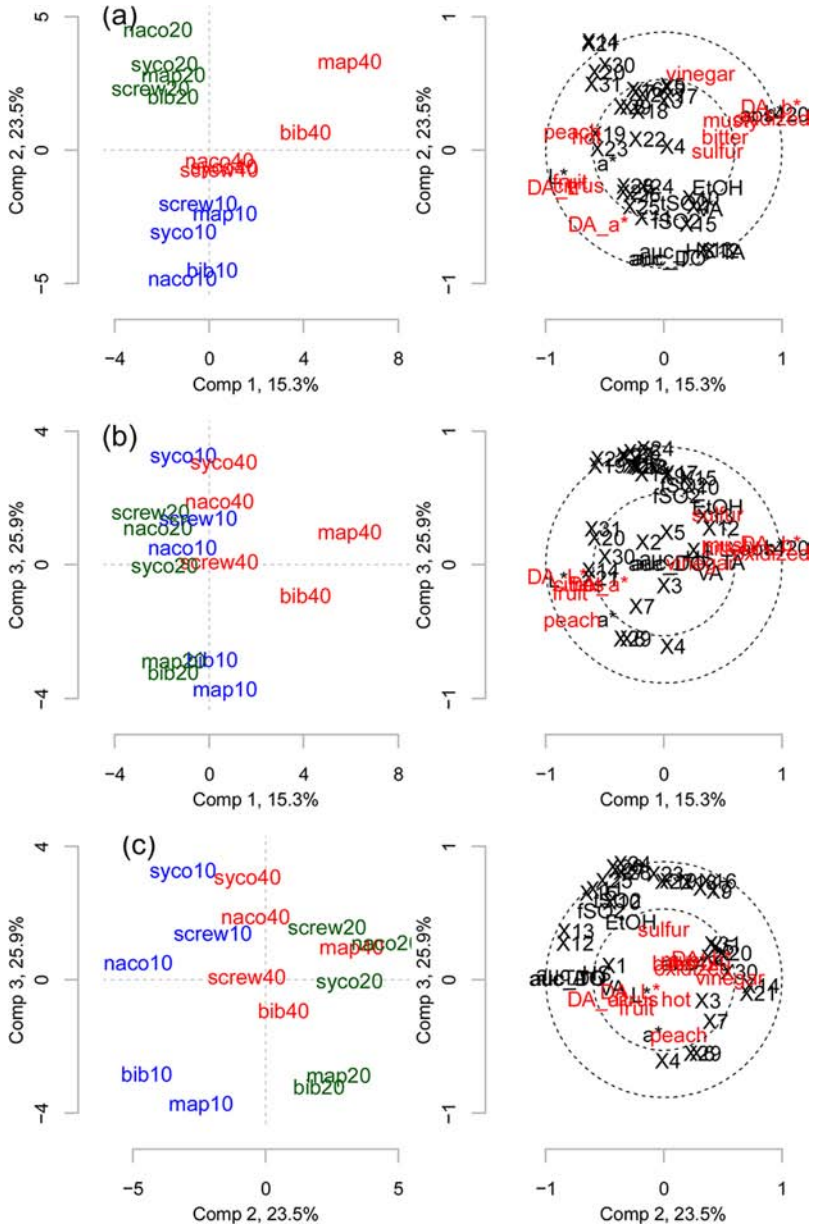

Figure 3. (a–c) PLS regressions of the white wine samples for the first three PLS dimensions. (a) First and second PLS dimensions, (b) first and third PLS dimensions, and (c) second and third PLS dimensions. Score and correlation plots are shown using the chemical and physical measurements (X matrix, variables colored in black) to predict the sensory attributes (Y matrix, variables colored in red). Sample and variable codes are listed in Tables 1 and 3.

The oxygen measurements (HS and DO) were statistically analyzed using a repeated measure ANOVA and were found to be significantly different for the packaging (P), temperature (T), and storage time (t) effects and the interactions t:P and t:T ($P \leq 0.05$). For the DO also, the other two interaction terms (P:T and t:T:P) were significantly different ($P \leq 0.05$). For further analyses, the AUC was calculated for the HS, DO, and TO consumption over the whole storage period and used these values as measures for the oxygen consumption, assuming that the faster the oxygen is consumed over time, the less oxygen is measured thus the smaller the AUC. As expected, the AUCs decreased with increasing storage temperature for all three measurements (AUC_HS, AUC_DO, and AUC_TO), independent of the packaging (see Table 1).

Correlation of all data using PLS Regression. As a last objective, the correlation between the sensory attributes and the chemical and physical measurements was studied using PLS. Within the first three dimensions of the PLS solution, nearly 65% of the predictor matrix variance could be explained with 15.3, 23.5, and 25.9% explained by the first, second, and third latent variable, respectively (Table 5). In the first dimension, the variances of the predicted sensory variables DA_*b** (sensory DA yellowness), DA_*L** (sensory DA lightness), and fruit, citrus, peach, and oxidized aromas were more than 50% explained, and using three latent vectors up to 94% of the variances of all predicted variables could be explained (see Table 5). Adding more latent vectors to the PLS model increased the root mean squared error of prediction (RMSEP) due to over fitting as shown in Figure 1 in the Supporting Information. For each variable, the RMSEP reached a minimum with two and three latent vectors.[48]

Plotting the first two PLS dimensions (Figure 3a), a clear separation of the samples based on their storage temperature was achieved with the 10 °C samples being located in the bottom left corner, showing a high positive correlation to the sensory variables fruit and citrus aroma, lightness (DA_L*), greenness (DA_a*), and the chemical/instrumental variables lightness (L*) (determined with the chromameter), the oxygen measures (AUC_HS, AUC_DO, and AUC_TO), TA, and the volatiles acetates X12, X13, and X15. The 20 °C samples were located in the top left corner and were sensorially characterized by peach aroma and hot mouthfeel, and the volatiles diethyl succinate, ethyl-3-methyl butanoate, the furfuryl ether, and TDN (X14, X21, X30, and X31). These samples showed no positive correlation to any other chemical measurements besides the mentioned volatiles (X14, X21, X30, and X31). For the 40 °C samples, a separation between the bottle and the BIB treatments was observed with the 40 °C bottle treatments being located in the center of the score plot, and the BIB samples (bib40 and map40) being located in the top right quadrant. The latter two samples showed a high correlation to the sensory attributes vinegar, oxidized, and yellowness (DA_b*) and the physical measures of yellowness (b*) and absorbance at 420 nm (abs420). Similar observations were made for the other two remaining dimensions shown in Figure 3b. Plotting the second and third dimension as shown in Figure 3c, samples were separated along the second dimension according to their packaging configuration (BIB at the bottom, bottle treatments at the top of the graph); all variables that showed a correlation of at least 60% (i.e., were located in between the inner and outer circle) were chemical measurements. Similarly to Robinson et al.,[20] various volatile compounds showed a strong positive correlation to storage temperature (i.e., positioned in between the 20 and 40 °C treatments), such as TDN (X31), 2-phenethyl alcohol (X9), ethyl-3-methyl butanoate (X21), various acids (X16–X18), and diethyl succinate (X14). In good agreement with previous works were also the negative storage temperature correlation of various esters (X15, X12, and X13) and terpenoid alcohols (X10 and X11), which showed the highest concentrations in the 10 °C samples. As expected, lightness (L*), green (a*), and yellow (b*) color showed all a high correlation to the respective sensory values determined by the panel, with the former two being highly associated with the sensory descriptors fruit and citrus for the 10 °C samples and the latter one being correlated to oxidized, musty, and vinegar attributes of the 40 °C samples.

In summary, storing unoaked Chardonnay in different packages significantly changes the sensory and chemical properties depending on the storage temperature. After a storage period of 3 months, bottle storage with various closures (natural cork, synthetic cork, and screw cap) changed the wine in a different way than BIB storage.

The largest changes were observed with the highest storage temperature of 40 °C, independent of the packaging. All studied samples showed signs of oxidation at the 40 °C storage temperature, described by the sensory panel as oxidized, musty, and sulfur, were lower in lightness and green color and higher in yellow color. Similarly, in the chemical analyses for color changes, volatile profiles, and basic chemical parameters, the 40 °C samples were darker and less green, showed an increase in yellow color and absorbance at 420 nm, and had lower amounts of free and total SO_2, ethanol, and lower TA. In the volatile pattern previously reported, oxidation and aging compounds increased in concentration, including diethyl succinate, TDN, and straight and branched alcohols, while fruit-related compounds such as acetates and terpenoids decreased with increasing storage temperature.

While in this study the storage temperature was a stronger driver of the observed changes and no significant sensory differences were found for the wine stored at 10 °C, the packaging type also influenced the properties of the wines: Especially the BIB samples showed severe and accelerated aging as compared to the three bottle treatments, which was significant for the two higher storage temperatures of 20 and 40 °C. Additionally, no significant differences were found in the sensory and chemical properties between the two BIB treatments, differing only in oxygen concentration during filling (bib and map). At lower storage temperatures, a slight, but not significant, tendency to less oxidation was found, but this effect was lost for the 40 °C storage temperature. It can be assumed that the used oxygen reduction was not sufficient enough to prevent or lower oxidation in the BIB samples during the 3 months of storage, and we recommend further research on this aspect.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Root mean squared error of prediction (RMSEP) plots (Supplementary Figure 1) and mean and standard deviation values for the 30 identified volatiles (Supplementary Table 1). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +1 530 752 9356. Fax: +1 530 752 0382. E-mail: hhopfer@ucdavis.edu.

Funding

Jerry Lohr provided postdoctoral financial support.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are indebted to Constellation Brands, Inc., for donating the wine samples and the synthetic corks and for help with the BIB filling with a special thank you to Glenn O'Dell and Zoran Ljepovic. ACI Cork USA, Inc., donated the natural corks. Charles "Chik" Brenneman, Paul Green, and Scott C. Frost helped with the bottling. The efforts and contributions of all members of the sensory panel are highly appreciated.

■ REFERENCES

(1) Zraly, K. *Windows on the World Complete Wine Course*, 25th ed.; Sterling: New York, NY, 2009.

(2) Michel, G.; Natalie, R.; Guillet, M.; Rodrigue, N. Shelf Life Testing Methodology and Data Analysis. In *Food Packaging and Shelf Life*; Robertson, G. L., Ed.; CRC Press: Boca Raton, FL, 2009; pp 31–53.

(3) 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.

(4) 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.

(5) 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.

(6) 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. *Aust. J. Grape Wine Res.* **2005**, *11*, 369−377.
(7) Reeves, M. J.; Malcolm, R. Packaging and the Shelf Life of Wine. In *Food Packaging and Shelf Life*; Robertson, G. L., Ed.; CRC Press: Boca Raton, FL, 2009; pp 231−257.
(8) Sundell, H. A.; Holen, B.; Nicolaysen, F.; Hilton, C.; Løkkeberg, Ø. Bag-in-box packaging for wine: Analysis of transport stress in barrier films. *Packag. Technol. Sci.* **1992**, *5*, 321−329.
(9) Lopes, P.; Saucier, C.; Teissedre, P.-L.; Glories, Y. Main Routes of Oxygen Ingress through Different Closures into Wine Bottles. *J. Agric. Food Chem.* **2007**, *55*, 5167−5170.
(10) Recognose Pty Ltd. Recognose Aroma Reference Technologies. http://www.aromadictionary.com/winearomas.html (accessed June 6, 2012).
(11) 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.
(12) Ramey, D. D.; Ough, C. S. Volatile ester hydrolysis or formation during storage of model solutions and wines. *J. Agric. Food Chem.* **1980**, *28*, 928−934.
(13) De La Presa-Owens, C.; Noble, A. C. Effect of Storage at Elevated Temperatures on Aroma of Chardonnay Wines. *Am. J. Enol. Vitic.* **1997**, *48*, 310−316.
(14) Gonzalez-Viñas, M. A.; Perez-Coello, M. S.; Salvador, M. D.; Cabezudo, M. D.; Martin-Alvarez, P. J. Changes in gas-chromatographic volatiles of young Airen wines during bottle storage. *Food Chem.* **1996**, *56*, 399−403.
(15) Leino, M.; Francis, I. L.; Kallio, H.; Williams, P. J. Gas Chromatographic headspace analysis of Chardonnay and Semillon wines after thermal processing. *Z. Lebensmitteluntersuchung Forsch. A* **1993**, *197*, 29−33.
(16) Marais, J.; Pool, H. J. Effect of storage time and temperature on the volatile composition and quality of dry white table wines. *Vitis* **1980**, *19*, 151−164.
(17) Recamales, A. F.; Gallo, V.; Hernanz, D.; Gonzalez-Miret, M. L.; Heredia, F. J. Effet of time and storage conditions on major volatile compounds of Zalema white wine. *J. Food Qual.* **2011**, *34*, 100−110.
(18) Pérez-Coello, M. S.; González-Viñas, M. A.; García-Romero, E.; Díaz-Maroto, M. C.; Cabezudo, M. D. Influence of storage temperature on the volatile compounds of young white wines. *Food Control* **2003**, *14*, 301−306.
(19) Makhotkina, O.; Pineau, B.; Kilmartin, P. A. Effect of storage temperature on the chemical composition and sensory profile of Sauvignon Blanc wines. *Aust. J. Grape Wine Res.* **2012**, *18*, 91−99.
(20) 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.
(21) Butzke, C. E.; Vogt, E. E.; Chacon-Rodriguez, L. Effect og heat exposure on wine quality during transport and storage. *J. Wine Res.* **2012**, *23*, 15−25.
(22) Shea, P.; Vialis, S.; Vidal, J.-C. Bag-in-Box Cone Meter. http://www.b-i-b.com/bib/web/downloads/O2BIBconeMeterBrochure29Nov2010.pdf (accessed June 1, 2012).
(23) Lawless, H. T.; Heymann, H. *Sensory Evaluation of Food: Principles and Practices*; Springer: New York, 2010.
(24) International Organization for Standardization. *ISO 3591: Sensory Analysis—Apparatus—Wine Tasting Glass*; 1977.
(25) Schanda, J. *Colorimetry: Understanding the CIE System*; John Wiley & Sons: New York, NY, 2007.
(26) International Organization for Standardization. *ISO 11664-4: Colorimetry—Part 4: CIE 1976 L*a*b* Colour Space*; 2008.
(27) Ough, C. S.; Amerine, M. A. *Methods Analysis of Musts and Wines*, 2nd ed.; J. Wiley: New York, 1988.
(28) Zoecklein, B.; Fugelsang, K. C.; Gump, B. H.; Nury, F. S. *Wine Analysis and Production*; Chapman & Hall: New York, NY, 1995.
(29) Abdi, H. Partial Least Squares (PLS) Regression . In *Encyclopedia of Social Sciences Research Methods*; Lewis-Beck, M., Bryman, A., Futing, T., Eds.; Sage Publications: Thousand Oaks, CA, 2003; pp 1−7.
(30) Haenlein, M.; Kaplan, A. M. A Beginner's Guide to Partial Least Squares Analysis. *Understanding Stat.* **2004**, *3*, 283−297.
(31) Geladi, P.; Kowalski, B. R. Partial Least-Squares Regression: A tutorial. *Anal. Chim. Acta* **1986**, *185*, 1−17.
(32) Lê, S.; Husson, F. Sensominer: A package for sensory data analysis. *J. Sensory Stud.* **2008**, *23*, 14−25.
(33) Le, S.; Josse, J.; Husson, F. F.; Lê, S. FactoMineR: An R Package for Multivariate Analysis. *J. Stat. Software* **2008**, *25*, 1−18.
(34) Mevik, B.-H.; Wehrens, R. The pls Package: Principal Component and Partial Least Squares Regression in R. *J. Stat. Software* **2007**, *18*, 1−24.
(35) R Foundation for Statistical Computing. *R: A Language and Environment for Statistical Computing*; R Foundation for Statstical Computing: Vienna, Austria, 2011.
(36) Gawel, R.; Sluyter, S. V.; Waters, E. J. The effects of ethanol and glycerol on the body and other sensory characteristics of Riesling wines. *Aust. J. Grape Wine Res.* **2007**, *13*, 38−45.
(37) Jones, P. R.; Gawel, R.; Francis, I. L.; Waters, E. J. The influence of interactions between major white wine components on the aroma, flavour and texture of model white wine. *Food Qual. Preference* **2008**, *19*, 596−607.
(38) Nurgel, C.; Pickering, G. J. Modelling of sweet, bitter and irritant sensations and their interactions elicited by model ice wines. *J. Sensory Stud.* **2006**, *21*, 505−519.
(39) Recamales, A. F.; Sayago, A.; Gonzalez-Miret, M. L.; Hernanz, D. The effect of time and storage conditions on the phenolic composition and colour of white wine. *Food Res. Int.* **2006**, *39*, 220−229.
(40) Chatfield, C.; Collins, A. J. *Introduction to Multivariate Analysis*; CRC Press: Boca Raton, FL, 1980.
(41) Polaskova, P.; Herszage, J.; Ebeler, S. E. Wine flavor: Chemistry in a glass. *Chem. Soc. Rev.* **2008**, *37*, 2478−2489.
(42) Dimkou, E.; Ugliano, M.; Dieval, J. B.; Vidal, S.; Aagaard, O.; Rauhut, D.; Jung, R. Impact of Headspace Oxygen and Closure on Sulfur Dioxide, Color, and Hydrogen Sulfide levels in a Riesling Wine. *Am. J. Enol. Vitic.* **2011**, *62*, 261−269.
(43) 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.
(44) Licciardello, F.; Del Nobile, M. A.; Spagna, G.; Muratore, G. Scalping of ethyloctanoate and linalool from a model wine into plastic films. *LWT—Food Sci. Technol.* **2009**, *42*, 1065−1069.
(45) Fukamachi, M.; Matsui, T.; Hwang, Y.-H.; Shimoda, M.; Osajima, Y. Sorption Behavior of Flavor Compounds into Packaging Films from Ethanol Solution. *J. Agric. Food Chem.* **1996**, *44*, 2810−2813.
(46) Acree, T.; Arn, H. Flavornet and human odor space Gas chromatography−olfactometry (GCO) of natural products. http://www.flavronet.org (accessed June 2, 2012).
(47) El-Sayed, A. M. The Pherobase: Database of Pheromones and Semiochemicals. http://www.pherobase.com (accessed June 1, 2012).
(48) 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.