

Study of Aged Cognac Using Solid-Phase Microextraction and Partial Least-Squares Regression

VIVIAN A. WATTS,[†] CHRISTIAN E. BUTZKE, AND ROGER B. BOULTON*

Department of Viticulture and Enology, University of California, Davis, One Shields Avenue, Davis, California 95616

Headspace solid-phase microextraction (SPME) and GC-MS were used to analyze 17 commercial French Cognac brandies (9 young and 8 well-aged, ranging in age from 3 to 55 years). Sixty-four volatiles were chosen on the basis of chromatographic separation and/or known odor importance. Chromatographic peaks were manually integrated and the peak area data analyzed using partial least-squares (PLS) regression to study relationships between volatile composition (X variables) and age (Y variable). When only those compounds with the highest significance were included and from these selected the variables (a total of 33) with the highest correlation loadings on the first two principal components, principal component 1 explained 82% of the variance of the measured compounds and 85% of the variance in age. These were considered the most important volatiles to distinguish products of different ages because young and old samples were separated along principal component 1. Norisoprenoids, terpenes, and acetate esters had weaker positive and negative loadings and were therefore left out. The PLS model could predict sample age accurately with the optimum 33 volatiles as well as with a smaller subset consisting of ethyl esters and methyl ketones.

KEYWORDS: Cognac; brandy; age; SPME; partial least-squares regression; PLS

INTRODUCTION

Cognac is often aged for a period of several decades, among the longest of any beverage or food. During the aging process, usually in partially filled oak barrels, physical and chemical processes occur that enhance the product's sensory qualities. Undesirable characteristics such as "hotness", "greenishness", and "rawness" almost always found in young distillates are diminished by aging, and the distillates develop flavors typical of matured spirits (*1*). Examples of such flavors are vanilla, spice, herbs, caramel, etc. The possibility for hundreds of reactions makes the study of such old products particularly interesting from a chemical viewpoint, yet challenging from a modeling perspective.

Evaporation of the two most abundant components, water and ethanol, causes a reduction in volume with time, and this contributes to increases in the concentration of all components. These concentrations, however, also depend on other factors such as the evaporation and also the formation and depletion reactions of these compounds such as oxidation, esterification, hydrolysis, and rearrangements. The concentration of any specific volatile component in an aging spirit is therefore the net result of these processes, and positive or negative correlations with age should be expected. The extraction of volatile (and nonvolatile) oak compounds also plays an important role in the

aging process (*2–4*), although these can vary considerably due to barrel conditions (wood type, manufacturing, condition, prior use, etc.).

As in the case of other foods and beverages, Cognac and other brandies have increasingly been studied with the development of new and more advanced analytical methods such as gas chromatography and mass spectrometry. Of particular interest was the identification of volatiles that may be involved in aging (*3, 5–7*) or attempts to accelerate the aging process (*8–13*), but the focus was predominantly on the relationships between oak chemistry and aging. There were fewer attempts to determine the effect of aging on overall brandy composition (*7, 14–16*), but none of these has analyzed changes in headspace composition.

Cognac brandy develops some highly desirable aromas after 15–20 years in barrels. These characteristic and desirable aromas are collectively known as "*rancio charentais*" (*5, 6*). Odd-numbered methyl ketones derived from fatty acids increase significantly during decades of aging and have been linked to this desirable Cognac characteristic (*5, 6*).

Early studies indicated that the concentration of some ethyl esters in experimental brandies increased with age in barrels, whereas the acetate esters of certain higher alcohols decreased (*7*). This is a result of the abundance of ethanol compared to other alcohols, which may drive the formation of ethyl esters or alternatively displace higher alcohols from their acetate esters to form ethyl acetate (transesterification). Acetic acid may also be extracted directly from oak (*7*) and forms by the oxidation

* Author to whom correspondence should be addressed [telephone (530) 752-0900; fax (530) 752-0382; e-mail rbboulton@ucdavis.edu].

[†] Fax 27 21 886 5414; e-mail vwatts@distell.co.za.

of ethanol via acetaldehyde in an oak environment (17), so that ethyl acetate, which is subject to variability in fermentation, distillation, and barrel oak composition, is not suitable as an aging indicator.

Other methods that have been used to predict brandy age include carbon-14 dating (18), with a reported accuracy of $\pm 5\%$, and content of furanic aldehydes such as furfural and 5-(hydroxymethyl)furfural as aging markers (19, 20). The latter method has been disputed because furanic aldehyde content depends not only on aging time in barrel but also on other factors such as barrel age and size and type of oak (7) and addition of caramel (21). In addition, part of the furfural present in brandy forms during distillation, so it cannot be used to indicate age (22). Postel and Adam found no correlation between furfural content and age (23).

Various statistical methods for the treatment of gas chromatographic data have been used to classify brandies and other distilled beverages. Multiple discriminant analysis was successfully used to classify French, German, and Cognac brandies (24). Fruit brandies and Cognacs could be differentiated from each other and from whiskies using a biometric method with correct classifications in most cases (25). Whiskies (Bourbon, Scotch, and "cheap Scotch") were differentiated well from each other when 70 compounds were used (25). Pattern recognition analysis was used to correctly classify samples as brandy or whiskey on the basis of their retention index chromatograms of organic acids (26).

The aim of this work was to use a simple and fast SPME method and partial least-squares (PLS) regression to predict sample age and separate Cognacs of different ages using only chromatographic peak areas. It proved to be successful in predicting Cognac age accurately using a relatively small number of volatiles easily detected by headspace SPME and GC-MS. This novel approach to study brandy aging using PLS and SPME will lay the foundation for further work, which may include the correlation of these results with sensory analysis. This method or a variation thereof could also be used to study the composition of other beverages and even foods.

MATERIALS AND METHODS

Samples. The 17 commercial Cognac samples were stored in the dark at 10 °C. Approximate and specific ages of these samples were obtained from a Cognac text (27), producers, and the Internet (company and dealer Internet websites). In cases of blends, the age was taken as the average of the ages of the blend components.

Sampling. A manual SPME holder (Supelco, Bellefonte PA) fitted with a fiber coated with 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) was used to study the headspace of the samples. All samples were diluted to 20% v/v ethanol by mixing 3 mL of Cognac and 3 mL of purified water (Millipore Q, Bedford, MA) in 10 mL glass vials. In a few cases, Cognac alcohol concentration was not exactly 40% v/v. In these cases it was necessary to adjust the ratio of Cognac and water slightly. The total sample volume, however, was always 6 mL. It was necessary to analyze all samples at exactly the same ethanol concentration because of the effect of ethanol on volatility of components. Furthermore, this 1:1 dilution is customary when spirits such as Cognac are judged. It reduces the harshness of the ethanol vapor, increases the volatility of aroma components, and makes it possible to appreciate the finer nuances of the spirit. Another reason for the dilution is to prevent the SPME fiber from being overloaded with ethanol, which is the most abundant volatile in the headspace. The vials were sealed with aluminum crimp-tops and Viton seals (Supelco) and allowed to equilibrate for 15 min in a water bath at the sampling temperature of 25 °C. Each sample was prepared and sampled individually to prevent samples from being in vials for different periods of time before analysis. Headspace sampling was performed for 30

Table 1. Reproducibility of Headspace SPME Method: Peak Areas of Four Methyl Ketones ($n = 6$): C7 = 2-Heptanone; C9 = 2-Nonanone; C11 = 2-Undecanone; C13 = 2-Tridecanone

	C7	C9	C11	C13
	580	3561	10038	4294
	573	3570	10335	4002
	570	3309	9896	3913
	506	3535	10554	4168
	604	3647	11258	4456
	584	3842	11335	4066
mean	569.5	3577.3	10569.3	4149.8
SD	33.3	172.6	608.5	199.9
CV (%)	5.85	4.83	5.76	4.82

min at 25 °C, after which the SPME fiber was retracted into its housing and inserted into the gas chromatograph inlet, where the volatiles desorbed onto the column.

GC-MS Analysis. Injections were splitless, and the split vent was opened 2 min after injection. The injector temperature was 240 °C, and an 0.8 mm SPME injector liner was used. Gas chromatographic analyses were performed using an Agilent 6890N gas chromatograph (Agilent, Palo Alto, CA). The column used was a 30 m HP-5ms capillary column with 0.25 mm i.d. and 0.25 μm stationary phase thickness. The oven temperature was kept at 40 °C for 5 min, followed by increases of 3 °C/min to 150 °C and then 5 °C/min to 220 °C, and held for 5 min. Helium was used as carrier gas, with an initial average linear velocity of 39 cm/s (1.2 mL/min). A head pressure of 8.9 psi was maintained throughout the analysis. GC-MS analysis was performed with an Agilent 5973 mass selective detector (Agilent) operated in electron impact mode (70 eV). The source temperature was 230 °C and the quadrupole temperature, 150 °C. The ion scan range was 39–320 amu (5 scans/s), and solvent delay was 4 min.

Quantitation. Absolute concentrations were not the object of this research, so peak areas were used for chromatographic data. Sixty-four compounds were chosen on the basis of their degree of chromatographic separation and/or sensory importance. Several classes of compounds were represented, including esters, ketones, alcohols, aldehydes, norisoprenoids, and terpenes. Chromatographic peaks were manually integrated. In cases where peaks overlapped, an ion that was not characteristic of the overlapping peak was extracted and integrated. This was done consistently across all samples. It should be noted that the method described here used only peak areas as a measure of liquid concentration. Vas et al. (28) followed a similar approach to follow ester generation during fermentation. In addition, we have determined that absolute concentration and peak area obtained by headspace SPME correlated well.

Statistical Analyses. The Unscrambler, version 7.6, statistical software (Camo, Woodbridge, NJ) was used in the data treatment. The method for modeling data was PLS1, which calculated how much of the variance found in one variable of interest (for example, a volatile or sample age) is explained by the variance in another group of volatiles. The validity of the PLS1 model was tested by determining its ability to predict sample age, using only SPME peak area data for 64 volatiles chosen to represent all major compound classes, including some of known odor importance. The technique of cross-validation was applied to determine the number of principal components (PCs) needed. During cross-validation, one sample at a time (of N samples) is left out, and the prediction ability is tested on the sample omitted. This is repeated N times resulting in N models and will give an estimate of the average prediction ability for the N models. This is then used, for example, to select the number of PCs needed.

Reproducibility was calculated by obtaining peak areas for four methyl ketones (six consecutive repetitions). Standard deviation and coefficient of variation (CV) were calculated and are given in Table 1.

Linearity was confirmed by using the headspace SPME method to sample four methyl ketones, ranging in concentration between 0 and 210 $\mu\text{g/L}$ in aqueous ethanol solutions.

Table 2. Slopes, Correlation Coefficients, Offsets, and Root Mean Square Errors (RMSEC) for Graphs of Predicted Age versus Measured Age, Using Different Sets of Volatiles

	slope	corr coeff	offset	RMSEC
all 64 volatiles	0.849	0.922	2.940	7.04
optimum 33 volatiles	0.996	0.998	0.081	1.17
4 methyl ketones	0.873	0.934	2.484	6.47
13 ethyl esters	0.948	0.974	1.007	4.12
ethyl esters + methyl ketones	0.974	0.987	0.516	2.95

RESULTS AND DISCUSSION

To study correlations between volatiles and age, PLS analyses were performed between volatiles (X variables) and age (Y variable). From the score plot, it was determined that the 17 Cognacs were separated according to their ages along PC1 (figure not shown).

The aim was to find a subgroup of volatiles which may be used to generate a PLS model that is able to accurately predict age. Prediction plots that show predicted age as a function of measured age were generated by the PLS software using different subgroups of volatiles.

It is important to keep in mind that, although concentration is probably the most important factor determining peak size, there are other physical phenomena that may also have an effect on peak size as determined by headspace SPME. It has been shown that the activity and therefore headspace concentration of hydrophobic aroma compounds is determined not only by their concentration but also by the presence of other hydrophobic volatiles in solution (29). Second, it is known that the volatility of aroma compounds may decrease through binding by polyphenols (30–32). Finally, headspace concentrations of long-chain fatty acid esters have been shown to be influenced by ethanol concentrations >20% v/v, a result of ethanol clusters into which the esters partition (33). In this project, however, ethanol concentration was always 20% v/v to eliminate this effect.

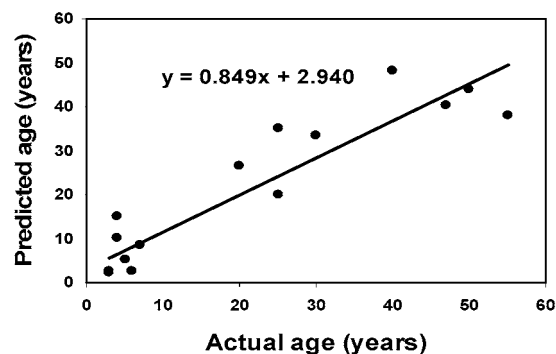
The method of headspace solid-phase microextraction is therefore very useful for the analysis of aroma because it selectively analyzes the headspace, the composition of which is the result of all the above-mentioned effects.

Following is a discussion of the ability of different classes of volatiles to predict age. Data are summarized in **Table 2**.

All 64 Variables. A PLS model was generated using the entire dataset of 64 chromatographic peak areas (X variables) as well as the approximate age (Y variable) for the 17 Cognac samples.

When this model was tested for its ability to predict age, 85% of the variance in age was explained and a graph of predicted age versus real age had a slope of 0.849 and a correlation coefficient of 0.922 (**Figure 1**), indicating less satisfactory age prediction. The increased scatter at lower ages is the result of less precise aging data for these VS Cognacs, which are typically blends of distillates aged between 2.5 and 7 years or sometimes more. It is therefore not easy to specify the exact average age of a VS blend with only the blend component ages given. This, however, did not have much of an effect on the slope.

Optimum Variables. Using the PLS software, the most significant variables (a total of 42) were identified, and from those a smaller subset of 33 was selected according to correlation loadings on PC1 and PC2. Only those volatiles for which >50% of the variance in age could be explained were included—a total of 33. These are listed in **Table 3**. The plot of predicted age versus actual age had a slope of 0.996 (**Figure 2**) and an offset

**Figure 1.** Predicted age versus actual age ($n = 17$) using PLS model with all 64 variables.**Table 3.** Optimum Volatile Compounds for Age Prediction of the 17 Cognac Samples According to PLS Analysis

retention time (min)	volatile compound	class	identification ^a	correlation with PC1 (age)
4.8	ethyl isobutyrate	ester	MS, RT	+
5.3	isobutyl acetate	ester	MS, RT	+
5.8	isoamyl formate	ester	MS	+
6.1	hexanal	aldehyde	MS, RT	+
8.4	ethyl 2-methylbutyrate	ester	MS, RT	+
8.5	ethyl isovalerate	ester	MS, RT	+
9.8	active amyl acetate	ester	MS	+
10.3	2-heptanone	ketone	MS, RT	+
10.9	ethyl pentanoate	ester	MS	+
16.4	ethyl hexanoate	ester	MS, RT	+
17	isoamyl butyrate	ester	MS	+
20.1	1-octanol	alcohol	MS, RT	+
21.2	2-nonanone	ketone	MS, RT	+
21.6	ethyl heptanoate	ester	MS, RT	+
21.8	nonanal	aldehyde	MS	+
22.3	phenethyl alcohol	alcohol	MS, RT	+
27	ethyl octanoate	ester	MS	+
29.3	active amyl hexanoate	ester	MS	+
29.5	isoamyl hexanoate	ester	MS	+
31.4	propyl octanoate	ester	MS	+
31.45	2-undecanone	ketone	MS, RT	+
31.6	ethyl nonanoate	ester	MS, RT	+
32.8	unknown lactone	lactone	MS	+
32.9	methyl decanoate	ester	MS, RT	+
34	isobutyl octanoate	ester	MS	+
35.9	ethyl 9-decanoate	ester	MS	+
36.4	ethyl decanoate	ester	MS	+
39.2	ethyl cinnamate	ester	MS, RT	+
40.4	propyl decanoate	ester	MS	+
40.5	ethyl undecanoate	ester	MS, RT	+
40.55	2-tridecanone	ketone	MS, RT	+
41.7	methyl dodecanoate	ester	MS	+
44.6	ethyl dodecanoate	ester	MS	+

^a MS, identification by mass spectrum only, thus tentative; RT, retention time.

of 0.081 years. These 33 compounds included 24 esters, 4 methyl ketones, 2 aldehydes, 2 alcohols, and an unknown lactone. Interestingly, all 33 of these had positive loadings on PC1; that is, they correlated positively with sample age. A possible reason for this is that volatiles that show negative correlations with age may change primarily during the early part of the aging process and therefore may not have appeared to be important because this analysis included samples with an age range of 3–55 years.

Of those that were not retained, about half had negative loadings on PC1. These included hexyl acetate, β -phenethyl acetate, d/l -limonene, two unknown terpenes, the norisoprenoids β -damascenone, vitispirane, and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), and an unknown norisoprenoid. Acetate esters may have lower concentrations in aged samples as a result of transesterification with ethanol, the most abundant alcohol present, displacing n -hexanol and phenethyl alcohol, respec-

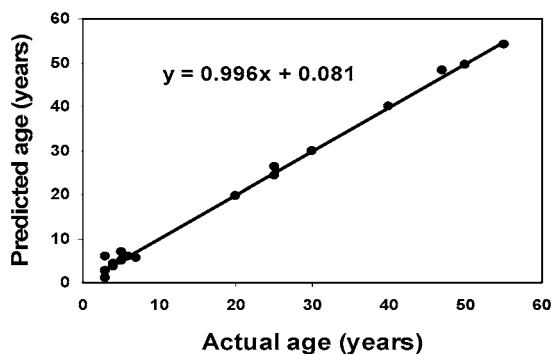


Figure 2. Predicted age versus actual age ($n = 17$) with optimum 33 volatiles.

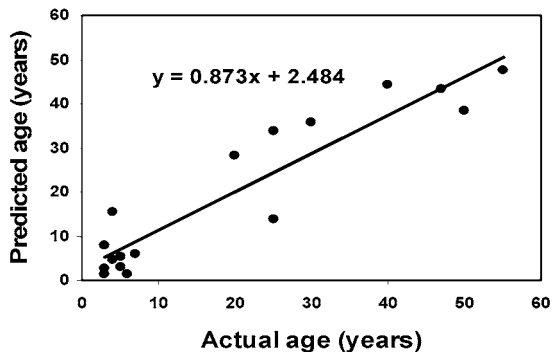


Figure 3. Predicted age versus actual age ($n = 17$) using PLS model with methyl ketone subset of 33 optimum volatiles.

tively. This was also reported and discussed by Onishi et al. (7). The terpenes and norisoprenoids may undergo acid-catalyzed rearrangements during aging, resulting in similar compounds with different odor characteristics. Rearrangements of this type are well-known in wine flavor chemistry (34, 35) and may explain the loss of such species.

Among the variables that were not retained, 3-hexen-1-ol, isoamyl octanoate, active amyl octanoate, and isobutyl decanoate seemed to correlate strongly with PC2. 3-Hexen-1-ol, and also to a lesser extent 1-octanol, 2-heptanone, and hexanal, had positive loadings, but isoamyl octanoate, active amyl octanoate, and isobutyl decanoate had highly negative loadings on PC2. We were unable to explain this separation.

It is important to keep in mind that these volatiles are not necessarily all odor-impact components; they are simply components that showed a strong relationship with age. Sensory research may be used to determine which of these volatiles are important odor-active components that are likely to contribute to the significant aroma differences between young and aged Cognacs.

Methyl Ketone Subset of Optimum 33 Variables. It had previously been determined that the four methyl ketones with odd-numbered chain lengths (2-heptanone, 2-nonanone, 2-undecanone, and 2-tridecanone) increase in concentration during extensive aging (5, 6, 36). The ability of a PLS model to predict age using only these compounds was therefore determined despite the small number of variables. Age prediction in this case was considerably less reliable, with a slope of 0.873 and a correlation coefficient of 0.934 (Figure 3). This lower R^2 value confirms our results when studying methyl ketone concentrations in relation with age (Watts, unpublished results), where graphs of liquid methyl ketone concentrations versus age also had a fairly high degree of scatter. Despite a clear increasing trend with age, the concentration of this small group of compounds,

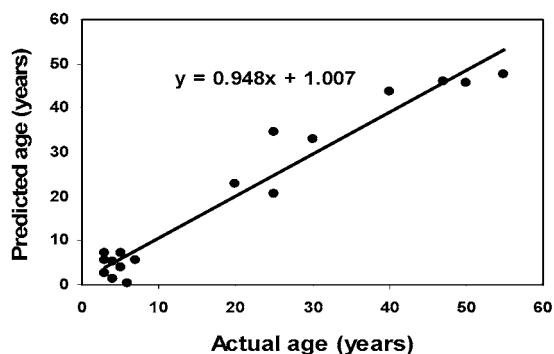


Figure 4. Predicted age versus actual age ($n = 17$) using PLS model with ethyl ester subset of 33 optimum variables.

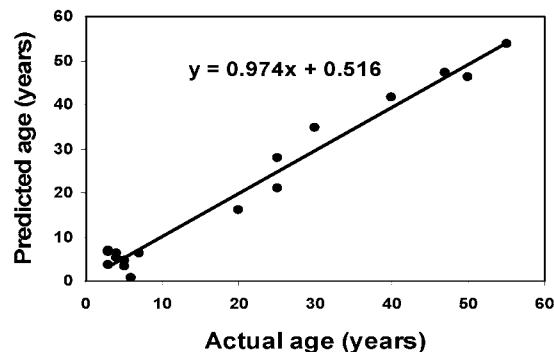


Figure 5. Predicted age versus actual age ($n = 17$) using PLS model with ethyl ester and methyl ketone subset of optimum 33 variables.

like all volatiles, is influenced by several factors that vary between producers such as fermentation conditions and distillation on yeast lees. These factors determine the initial concentrations of volatiles and/or their precursors. It is therefore better to use more volatiles from different classes of compounds for reliable age prediction as seen in the previous section.

Ethyl Ester Subset of Optimum 33 Variables. When the 13 ethyl esters were taken from the 33 optimum volatiles, the resulting PLS model predicted age better than in the case of the 4 methyl ketones. The slope of the prediction graph was 0.948, the offset 1.007, and the correlation coefficient 0.974 (Figure 4).

One reason for the ethyl esters being able to predict age more accurately than the methyl ketones is that the ethyl ester subset included 13 variables, whereas the methyl ketone subset included only four variables. More variables will likely lead to an improved PLS model. Second, the concentrations of these two classes of volatiles in Cognac depend on different factors during aging. Methyl ketones appear to be formed through a radical mechanism requiring oxygen to produce hydrogen peroxide in the presence of copper ions (Watts, unpublished results), whereas ester content requires hydrogen ions and ethanol. A possible reason for the difference in the ability to predict age may be that the variation of the factors influencing methyl ketone formation (yeast lees during distillation, copper ions, phenolic content, and oxygen content) is greater than those involved in ester formation.

Ethyl Ester and Methyl Ketone Subset of Optimum 33 Variables versus Age. A PLS model including the ethyl esters as well as the methyl ketones is significantly improved compared to either of the two alone. The prediction graph had a slope of 0.974, an offset of 0.516, and a correlation coefficient of 0.987 (Figure 5). These 17 variables are therefore able to predict age with a higher degree of accuracy than in the case of the ethyl

esters alone, the accuracy approaching that obtained with the optimum 33 compounds included.

Conclusions. Gas chromatographic peak area data for volatiles, obtained with solid-phase microextraction coupled to GC-MS and analyzed with PLS regression is a suitable method to distinguish between young and extensively aged Cognacs. The subset consisting of 17 volatiles (13 ethyl esters and 4 methyl ketones) could predict sample age with a high degree of accuracy. It therefore appears that esterification in addition to methyl ketone formation may be two of the most important processes in the aging of Cognac over a long period. Further work is needed to determine which of the volatiles that have been highly correlated with age are in fact significant at a sensory level. This method may also prove to be applicable to the analysis of other foods and beverages.

ACKNOWLEDGMENT

We thank Bob Emmons for donating Cognac samples.

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Received for review March 26, 2003. Revised manuscript received July 31, 2003. Accepted August 3, 2003.