Chemical Markers for Tracking the Sensory Contribution of Production Stages in Muscat Wine Distillates

MARCIAL PEÑA Y LILLO, EDUARDO AGOSIN, ANDREA BELANCIC, AND ERIC LATRILLE

ABSTRACT: The main sensory contribution of each post-fermentation production stage of muscat wine distillates can be tracked by following the concentration of just 1 corresponding chemical marker. Matching sample clusters of sensory and chemical data by using principal components analysis (PCA) revealed potential chemical markers. The data used in this study correspond to 12 sensory attributes that showed significant differences among products ($P < 0.05$) and concentrations of 23 volatile compounds of 14 distillate fractions and 15 finished Piscos. Artificial fruit attribute, characteristic of the head fraction (FR1) can be tracked with esters. Linalool, main odor attribute of the 1st part of the heart (FR2) can be tracked with linalool molecule. The 2nd part of the heart (FR3) can be tracked with octanoic acid, decanoic acid, furfural and ethyl lactate, accounting for tails attribute. In blended and aged finished products, chemical markers accounting for the effects of distillate fractions were similar but not identical to the markers from samples obtained from the purely distilled samples. Chemical markers for FR1 are ethyl hexanoate, ethyl octanoate, ethyl decanoate. Differentiation between FR1 and FR2 is less evident than in the purely distilled samples due to the linalool and artificial fruit attribute correlation. Chemical markers for FR2, therefore, include linalool and esters ethyl hexanoate, ethyl octanoate, and ethyl decanoate. The blending of the 2nd part of the heart (FR3) can be tracked with 2-phenylethanol, ethyl lactate, and decanoic acid. Oak aging was tracked with eugenol and whisky lactones, while 5-hydroxy-methyl-2-furfural accounted for added caramel.

Keywords: distillate fraction, blending, production stage, principal components, clustering

Introduction

Pisco is highly popular and produced almost entirely in Peru and Chile where it is the most widely consumed spirit. In this Muscat wine distillate, more than 50 aroma compounds such as esters, acids, alcohols, aldehydes, and terpenes have been identified in gas chromatography-mass spectrometry (GC-MS) of non-aged spirits (Herraiz and others 1990). A study involving 8 aroma compounds has shown 6 to be probable sensory impact molecules (Peña y Lillo and others 2003). However, no formal study to determine sensory impact molecules, directly responsible for a perception, has been developed yet for Chilean Pisco. In another study, an expert panel distinguished 42 olfactory attributes in this spirit, further highlighting the complexity of the product (Bordeu and others 2004).

Food producers seek sensory differentiation in their products to satisfy consumer preferences and ensure product quality. Food production involves a series of specific processes, many of which amend sensory attributes and chemical composition. Pisco's aroma compound content is altered at several production stages. Muscat grapes contain high concentrations of terpenes (Bayonove and Cordonnier 1971; Marais 1983; Baumes and others 1994), although terpene profiles vary from 1 variety to another (Gunata and others 1985; Agosin and others 2000) and may differ depending on numerous factors, the most significant of which are sun exposure (Belancic and others 1997) and harvest conditions (Reynolds and others 1993). C6 compounds mostly originate in grape crushing and pressing (Bayonove and others 2000). Wine fermentation mostly synthesizes alcohols, esters, and acids (Etiévant 1991; Lambrechts and Pretorius 2000).

Post-fermentation production processes include distillation, blending, oak aging, and the addition of caramel. Previous works offer some insight into these processes. In distillation, for example, high ester concentrations have been found in the head fraction, whereas the 1st part of the heart is rich in alcohols and terpenes; acids, alcohols, and aldehydes abound in the 2nd part of the heart (Peña y Lillo and others 2003). Furfural is a product of distillation (Jeurings and Kuppers 1980; Quesada Granados and others 1996). Oak aging, which adds several chemical species, such as lactones, vanillic derivatives, and phenolic compounds, has also been studied extensively for wines and spirits (Mosedale and Puech 1998; Chatonnet 1999). Pisco producers currently differentiate their products using these post-fermentation production processes.

Monitoring sensory impact molecules are a means of tracking the sensory contribution of food-production processes. Nonetheless, foods are complex mixtures; many molecules may be responsible for a given sensory attribute. Moreover, current experimental procedures for identifying sensory impact molecules are costly and time-consuming, making monitoring the different stages of a food-production process for the most part impracticable. Our proposal is that volatile molecules, which correlate well with the sensory contribution of the different stages of production, provide a viable alternative to sensory impact molecules because they comprise fewer compounds and hence allow faster quantification. This

MS 20040473 Submitted 7/13/04, Revised 2/18/05, Accepted 5/20/05. *Author Peña y Lillo is with Beverages Global Innovation Center, Unilever R&D Colworth, Bedford, U.K., MK44 1LQ. Author Agosin is with Dept. de Ingeniería Química y Bioprocesos, Pontificia Univ. Católica de Chile(PUC), Vicuña Mackenna 4860, Macul, Santiago, Chile. Author Belancic is with Centro de Aromas, DICTUC SA, Vicuña Mackenna 4860, Macul, Santiago, Chile. Author Latrille is with INRA, Laboratoire de Biotechnologie de l'Environnement Avenue des Etangs, 11100 Narbonne, France. Direct Inquiries to author Agosin (E-mail: agosin@ing.puc.cl).*

approach for obtaining and applying chemical markers of a given sensory perception differs from classical usage of chemical markers, such as in the determination of the appellation of Californian wines (Arrhenius and others 1996).

The aim of this study is to find chemical markers for tracking the sensory contribution of the 3 post-fermentation stages of Chilean Pisco: distillation, blending, and aging. We approach the problem using multivariable statistical methods to process data from sensory and chemical analysis and by applying heuristics for matching the sensory and chemical differentiation of samples.

Materials and Methods

Samples

Different distillations produced fractions of Muscat wine distillate, as previously reported (Peña y Lillo and others 2005). These fractions correspond to head (FR1), the 1st part of the heart (FR2), and the 2nd part of the heart (FR3). In total, 14 samples were collected, 5 FR1 samples, 4 corresponding to FR2 and 5 to FR3; none of these were processed further.

In addition, 15 finished Piscos were commercially available and came from 2 major Chilean distilleries, A (product codes been A1, A2, A3, A4, and A5) and B (B1, B2, B3, B4, and B5), and from smaller independent distilleries, IND (IND1, IND2, IND3, IND4, and IND5). These samples were subjected to standard production procedures: blending, oak-aging, and the eventual addition of caramel.

Sensory analysis

Odor profile data (orthonasal perception obtained by sniffing the samples) were obtained for all the samples by means of descriptive analysis, as previously reported (Peña y Lillo and others 2005). Four women and 8 men (aged 24 to 38 y, mean age 29 y) from the Catholic Univ. of Chile participated in the study. All subjects were Pisco consumers; 8 of them had no previous experience in sensory analysis, and 3 subjects were enologists (2 professionals and 1 student). The subjects agreed on a common vocabulary of 13 attributes of the Pisco Wheel (Bordeu and others 2004). They were trained in the good use of the vocabulary by smelling the standards defined for the Pisco Wheel and familiarized with the structured 8-category intensity scale (0 denoting an absence of the considered perception and 7 denoting a very intense perception). Six samples were tested per session and presented in a randomized order to the subjects (finished Piscos and distillation fractions were distributed homogeneously over all the sessions). Ten of the 29 products were replicated 3 times to assess panel and subject performance. Odor profile data were analyzed with a 2-factor analysis of variance with interaction (product, subject as random factor). $P < 0.05$ indicated significant difference among samples. ANOVA was performed using SAS software package (SAS Inst. 1990).

Chemical analysis

Samples were diluted to 20% v/v ethanol and extracted with dichloromethane. One hundred milliliters of the diluted sample with 100 μL of the internal standard (4-nonanol 3.6 mg/mL) was poured into 250-mL centrifuge flasks (polypropylene) and cooled in an ice bath under nitrogen. Dichloromethane (25 mL) was added, and the mixture was stirred during 30 min at 700 rpm. The organic phase was separated by centrifuging for 15 min at 5000 rpm (4 °C). The sample was re-extracted with dichloromethane (25 mL), stirred, and centrifuged. The organic phases were poured together, dried over sodium sulfate, and concentrated by distillation through a Vigreaux and then Dufton column at 47 ° to 1 mL (Kotseridis and Baumes 2000). Each extraction was done in triplicate. Finally, 2 μL of the extracted sample was injected into an HP 6890 gas chromatograph (Hewlett Packard, Palo Alto, Calif., U.S.A.) to separate and identify volatile compounds. The latter was equipped with a split/splitless injector, a polar polyethyleneglycol packed column (30 m × 0.25-mm inner dia; 0.25 bonded phase, HP-FFAP) and a mass spectrometer (HP 5972). Operating conditions for the distillate fractions were as follows: mass detector temperature, 280 °C; injector temperature, 60 °C; temperature program held at 60 °C for 3 min and then increased at a rate of 3 °C/min up to 235 °C where it was finally held for 5 min. Operating conditions for the finished Piscos were as follows: mass detector temperature, 280 °C; injector temperature, 250 °C; temperature program held at 35 °C for 5 min and then increased at a rate of 1 °C/min up to 60 °C where it was held for 1 min. Next, the temperature was increased at a rate of 0.5 °C/min up to 65 °C and then at a rate of 3 °C/min up to 230 °C, and held constant for 15 min.

We identified a reduced set of volatiles, which was selected to cover the entire spectra for non-aged Pisco spirits found by Herraiz and others (1990). Furthermore, molecules frequently reported as products of aging in wines and other spirits were also identified. Identification was carried out with the NIST/EPA/NIH library of 130000 spectra.

Data analysis

Principal component analysis (PCA) was performed on the sensory attributes showing significant differences among samples ($P < 0.05$), using R 1.2.2 for Windows (http://www.r-project.org/). In this technique, principal components are constructed using linear combinations of the original variables. These components maximize data variance and constitute an orthogonal space. Before analysis, odor data were centered but not normalized. Consequently, principal components were calculated from the covariance matrix because the same scale was used to measure all sensory attributes.

Chemical data were analyzed with PCA using the correlation matrix (data centered and normalized) because concentrations differed significantly among the compounds identified.

Heuristic method for determining chemical markers

A heuristic clustering procedure was applied to distillate fractions for studying the distillation process and to finished Piscos for studying blending and aging.

PCA was 1st applied to odor data. Two graphs were obtained for each pair of principal components, 1 with sample scores and the other with the variable loadings. Those principal components summing at least 80% of the total variance were retained; single components that add considerably less variance than its predecessor were rejected.

In our case study, principal component analysis for odor data resulted in 2 principal components being retained (in both distillate fractions or finished Piscos). Sample clustering was then carried out by inspecting the 2-dimensional score PCA graphs to obtain "sensory clusters."

PCA was then applied to chemical data. Principal components were selected as described previously, and all of those retained were plotted.

Sample clusters were identified as described previously. Samples within a "sensory cluster" were sought within the "chemical clusters." Upon successful cluster matching, only chemical compounds having the highest correlations with a sensory attribute characterizing a "sensory cluster" were retained. These molecules were identified as chemical markers when they were linked to a specific post-fermentation production process: distillation, blending, and aging.

For the blending process, identification of chemical markers not only contemplate those molecules indicated by the heuristic procedure applied to finished Piscos, but also specific chemical markers identified in the distillation of each fraction.

Table 1—Chemical markers for post fermentation production processes in Pisco[a,b,c,d]

Distillation and blending process	Sensory attribute: main sensory note	Ethyl hexanoate	Ethyl octanoate	Ethyl decanoate	Hexyl acetate	Isoamyl acetate	Linalool	Geraniol	1-Hexanol	2-Phenyl-ethanol	Ethyl lactate	Octanoic acid	Decanoic acid	Furfural
FR1	Artificial fruit	**0.96**	**0.93**	**0.88**	**0.93**	**0.94**	NA	NA	NA	NA	NA	NA	NA	NA
FR1 post-blending	Artificial fruit	**0.88**	**0.85**	**0.84**	0.47	0.32	NA	NA	NA	NA	NA	NA	NA	NA
FR2	Linalool	0.53	0.49	0.48	0.5	0.5	**0.78**	0.14	0.82	NA	NA	NA	NA	NA
FR2 post-blending	Linalool	**0.74**	**0.7**	**0.71**	0.48	0.54	**0.48**	0.28	0.13	NA	NA	NA	NA	NA
FR3	Tails	NA	NA	NA	NA	NA	NA	NA	NA	0.34	**0.56**	**0.69**	**0.61**	**0.80**
FR3 post-blending	Tails	NA	NA	NA	NA	NA	NA	NA	NA	**0.65**	**0.78**	0.27	**0.51**	0.11

Aging processes	Main sensory note	Eugenol	Whisky lactone *cis*	Whisky lactone *trans*	5-hydroxy-methyl 2-furfural
Oak aging	Oak	**0.80**	**0.67**	**0.73**	NA
Caramel addition	Oak	NA	NA	NA	**0.34**

[a]Correlation coefficients between the sensory attributes and chemical markers of distillation, blending, and aging processes.
[b]NA = not applicable.
[c]Bold text indicates the compound is a chemical marker.
[d]FR1, FR2, FR3 correlations were calculated using 14 samples of distillate fractions. Post-blending FR1, FR2, and FR3, oak aging, and caramel addition correlations were calculated with 15 samples of finished products.

Results and Discussion

Chemical identification of volatile compounds

We identified a reduced set of volatiles, which was selected to cover the entire spectra for Pisco spirits. The compounds identified (CAS numbers in parentheses) were as follows: 1-hexanol (111-27-3), 2-phenylethanol (60-12-8), *cis*-3-hexen-1-ol (928-96-1), octanoic acid (124-07-2), decanoic acid (334-48-5), isoamyl acetate (123-92-2), ethyl hexanoate (123-66-0), ethyl lactate (97-64-3), ethyl octanoate (106-32-1), ethyl decanoate (110-38-3), 2-phenylethyl acetate (103-45-7), hexyl acetate (142-92-7), linalool (78-70-6), geraniol (106-24-1), furfural (98-01-1). A further 8 compounds, which were not found in distillate fractions, were identified in finished Piscos: Whiskylactone-*trans* (CAS number for *cis* and *trans* whisky lactone is 39212-23-2), whiskylactone-*cis* (55013-32-6), eugenol (97-53-0), vanillin (148-53-8), ethyl vanillin (121-32-4), vanillin derivate, guaiacyl ketone (2503-46-0), and 5-hydroxy-methyl-2-furfural (67-47-0). Analytical data of all of the samples are available in the Appendix (Table A.1 and A.2).

Sensory analysis

Of the 13 sensory attributes, 12 showed significant differences among samples: acetaldehyde, tails (associated with Pisco distillation tails, that is, the last distillation cut recovered), acetic acid, ethyl acetate, oak, caramel, vanilla, raisins, citrus, artificial fruit (associated to artificial fruit juice), linalol, and hay. The mean score for each discriminant attribute and each sample can be found in the Appendix (Table A.3).

Distillation

PCA was performed on the odor notes of distillate fractions (Figure 1). The 1st 2 principal components cover 93.44% of the variance; the PC1 axis opposing tails against artificial fruit and linalool and the PC2 axis negatively loaded with ethyl acetate attribute. The 3 distillate fractions are clearly differentiated. FR1 presents high intensities of the artificial fruit attribute, FR2 fraction presents high intensities of linalool and citrus notes, and FR3 presents high intensities of tails. These 4 attributes were the main sensory characteristics describing the distillation fractions (Table 1).

Three principal components of the PCA for chemical composition were required to represent 89.6% of the variance of distillate fractions. Figure 2 shows that PC1 axis opposes 2-phenylethyl acetate, ethyl lactate and the acids (octanoic acid and decanoic acid) to the esters (isoamyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, hexyl acetate). The PC2 axis opposes furfural with the terpenes (geraniol and linalool) and alcohols (1-hexanol and *cis*-3-hexen-1-ol). The FR1 fraction had high concentrations of hexyl acetate, ethyl decanoate, ethyl octanoate, ethyl hexanoate, and isoamyl acetate. The FR2 fraction had high concentrations of linalool, geraniol, *cis*-3-hexen-1-ol, and 1-hexanol, and the FR3 fraction had high concentrations of octanoic acid, decanoic acid, furfural, ethyl lactate, and 2-phenylethanol. Therefore, these 14 compounds were considered potential chemical markers for describing distillate fractions.

The PC3 axis differentiates products according to their high 2-phenylethanol content (results not shown). It clusters 1 FR2 and 1 FR3 sample together. Because these samples were not differentiated in the corresponding sensory map, we did not consider this principal component for determining markers.

Sensory attributes and their associated chemical markers are summarized in Table 1 with their respective correlation coefficients. The FR1 fraction associated molecules (discussed previously) had high correlations with artificial fruit (r close to 0.9). Molecules associated with FR2, linalool, geraniol, and 1-hexenol, presented r coefficients of 0.78, 0.14, and 0.82, respectively, with the linalool attribute. In addition, molecules associated with FR1, ethyl decanoate, ethyl octanoate, ethyl hexanoate, hexyl acetate, and isoamyl acetate, had correlations with linalool attribute of $r = 0.48$, $r = 0.49$, $r = 0.53$, $r = 0.5$, and $r = 0.5$, respectively. Tails sensory attribute and molecules associated with FR3 had its highest correlation value for furfural ($r = 0.8$), whereas phenylethanol ($r = 0.34$), ethyl lactate ($r = 0.56$), octanoic acid ($r = 0.69$), and decanoic acid ($r = 0.61$) presented smaller correlation coefficients.

Blending

Only finished products were evaluated at this stage, and PCA was performed on their odor intensities and on their chemical concentrations. Figure 3 shows PCA applied to finished Pisco odor notes. The 1st 2 principal components cover 85% of the variance. The PC1 axis opposed tails and acetaldehyde with linalool odor. The PC2 axis opposed artificial fruit with oak, which was correlated with caramel and vanilla notes. Here, we will just focus on distillate fraction associated clusters (as indicated in the previous section).

A2 and A5 Piscos had high intensities of linalool and citrus notes; A1, A3, and A4 Piscos had high intensities of artificial fruit and citrus. Moreover, artificial fruit, linalool, and citrus were correlated. IND2, IND3, IND4, IND5, and B2 Piscos had high intensities of tails, ethyl acetate, and acetaldehyde attributes.

Figure 4 and 5 show PCA performed on the chemical composition of finished Piscos (23 volatile molecules identified). Five principal components were required to represent more than 85% of the data variance. Figure 4 shows the 1st 2 principal components, in which the PC1 axis opposed 2-phenylethanol and ethyl lactate with ethyl octanoate, ethyl hexanoate, ethyl decanoate, octanoic acid, decanoic acid, vanilline, vanilline derivative, ethyl vanilline, guaiacyl ketone, and whisky lactones (*cis* and *trans*). The PC2 axis opposed 2-phenylethanol, ethyl lactate, and furfural with linalool, isoamyl acetate, and hexyl acetate. The map of Figure 4 clusters IND2, IND3, IND4, and IND5 samples, which had high concentrations of ethyl lactate and 2-phenylethanol. A2, A5, and B4 samples showed high concentrations of whisky lactone, vanilline, vanilline derivative, ethyl vanilline, guaiacyl ketone, octanoic

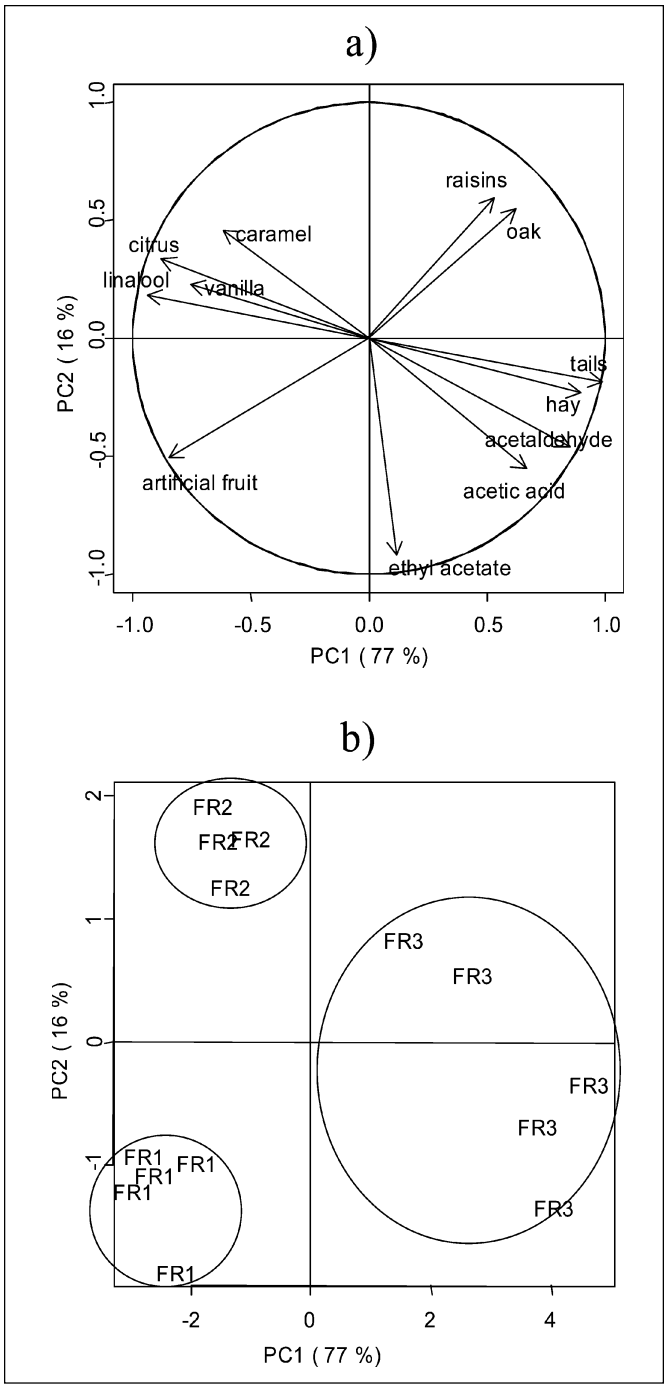

Figure 1—1st 2 principal components calculated with odor intensities of distillate fractions. (a) correlation circle shows variable loadings; (b) sample scores.

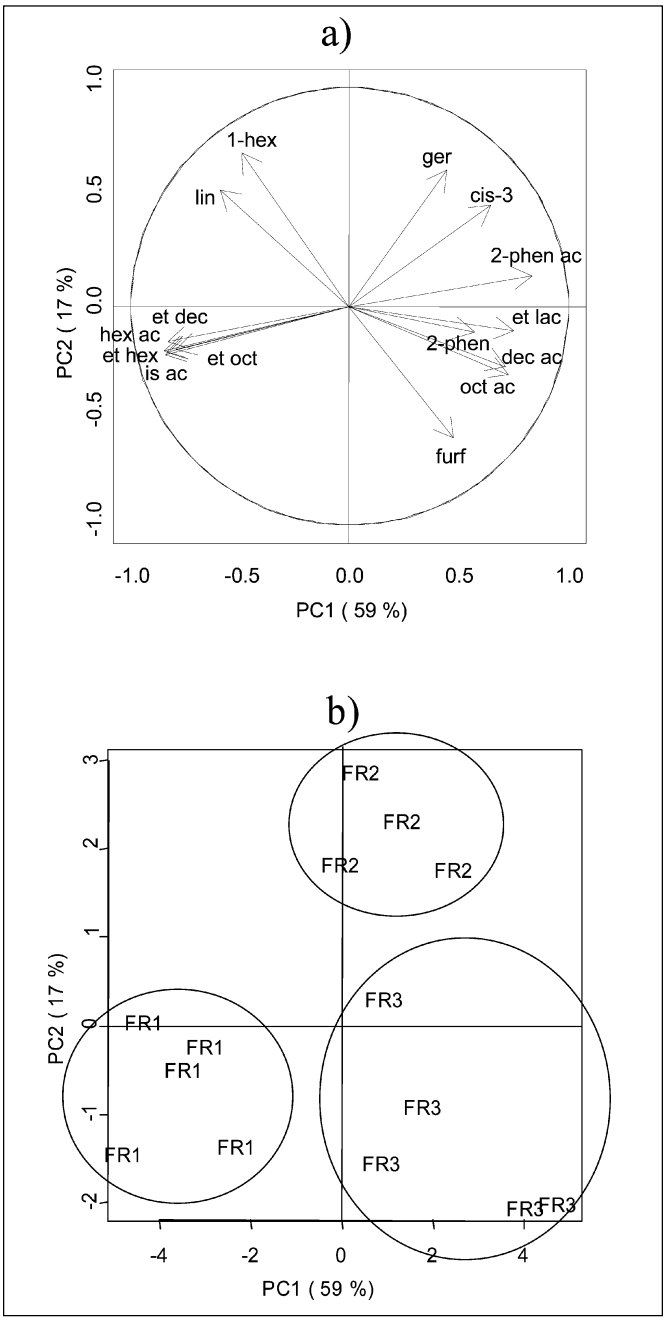

Figure 2—1st 2 principal components calculated with volatile compounds of distillate fractions. (a) variable loadings in the correlation circle; (b) sample scores. 1-hex = 1-hexanol; 2-phen = 2-phenylethanol; 2-phen ac = 2-phenylethyl acetate; *cis*-3 = *cis*-3-hexen-1-ol; dec ac = decanoic acid; et dec = ethyl decanoate; et hex = ethyl hexanoate; et lac = ethyl lactate; et oct = ethyl octanoate; fur = furfural; ger = geraniol; hex ac = hexyl acetate; is ac = isoamyl acetate; lin = linalool; oct ac = octanoic acid.

acid. A1, A3, and A4 had high concentrations of hexyl acetate, isoamyl acetate, and linalool. B1, B2, B3, B5, and IND1 samples appeared close to the intersection of both principal components.

In Figure 5, the PC3 axis opposed ethyl octanoate, ethyl decanoate, and ethyl hexanoate with eugenol, 2-phenylethyl acetate, 1-hexanol, and the whisky lactones (*cis* and *trans*). Samples differentiated according to distillate fraction markers were Piscos A (specially A2, A5) showing high concentrations of esters (except ethyl lactate) and octanoic acid and decanoic acid and IND2, IND 3, IND 4, and IND 5 Piscos had high concentrations of ethyl lactate.

The PC4 axis differentiated samples according to the aging process and hence is presented in the next section.

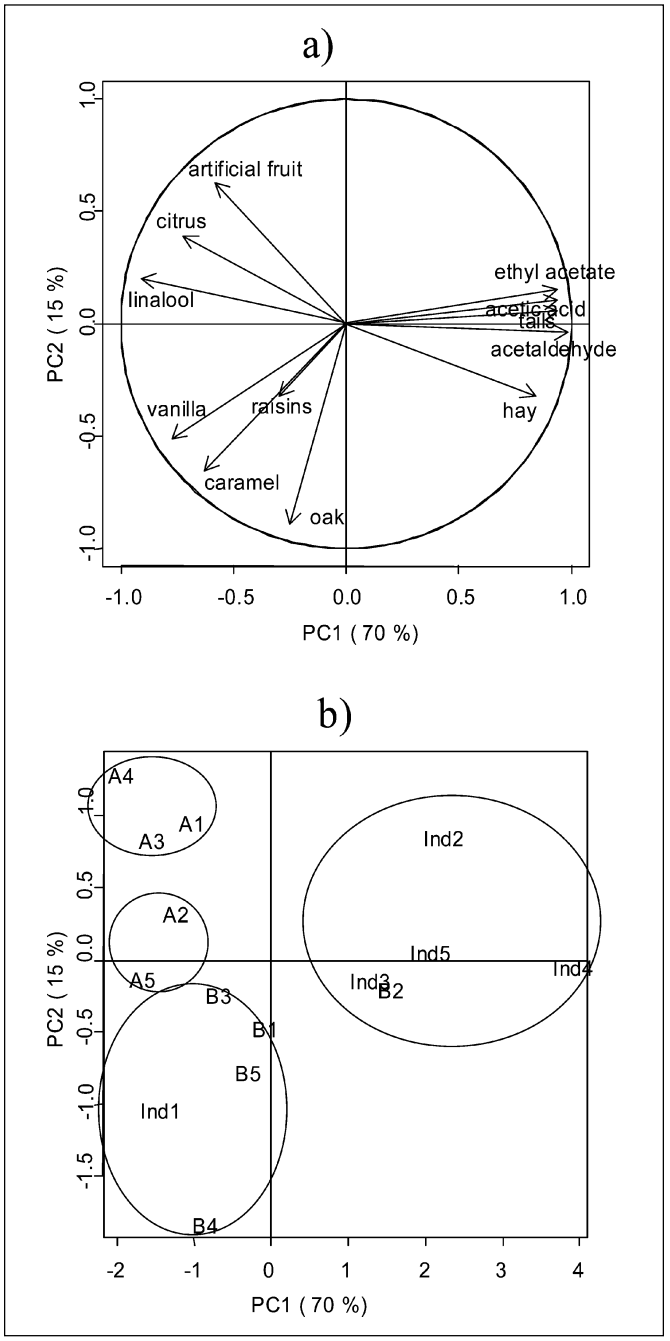

Figure 3—1st 2 principal components calculated with odor intensities of finished Piscos. (a) variable loadings in the correlation circle; (b) sample scores.

The PC5 axis indicated that IND3 has high concentration of geraniol, but because this sample was not differentiated from the others by its odor profile, this component was ignored (result not shown).

Blending-associated sensory attributes and the correlations with their associated molecules (calculated solely using finished Piscos) are reported in Table1. This table includes not only those molecules

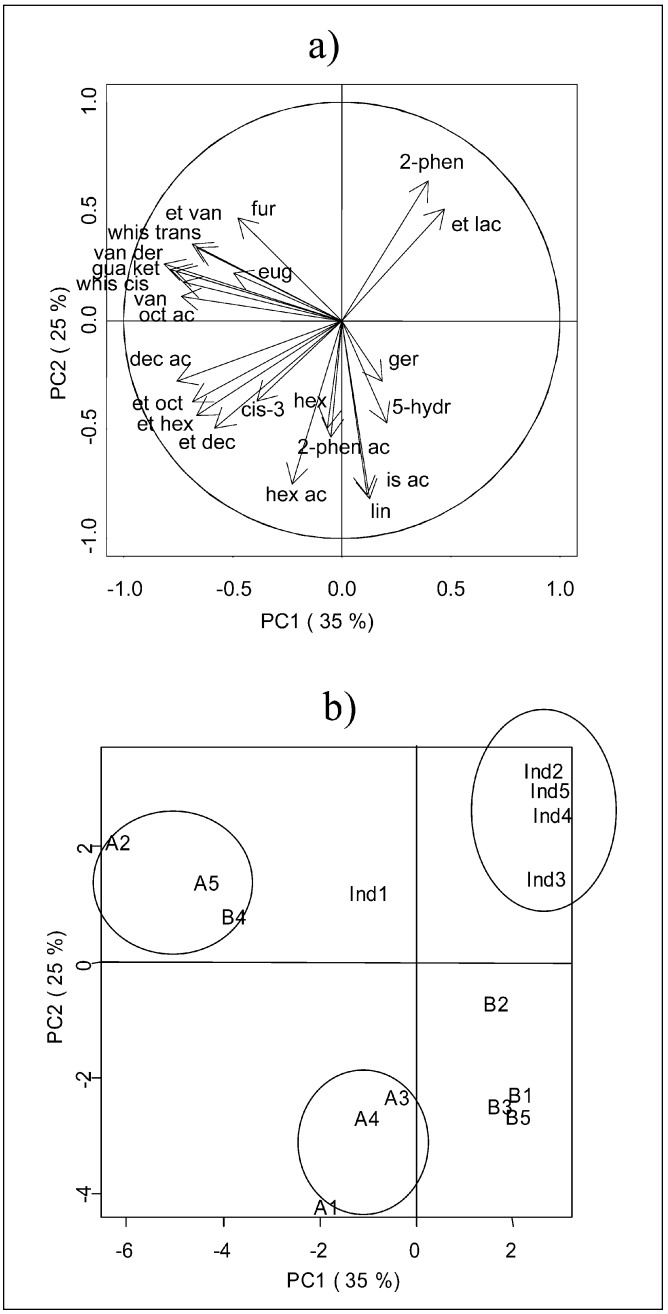

Figure 4—1st 2 principal components calculated on 23 chemical compounds of finished Piscos. (a) variable loadings in the correlation circle; (b) sample scores. 1-hex = 1-hexanol; 2-phen = 2-phenylethanol; 2-phen ac = 2-phenylethyl acetate; 5-hydr = 5-hydroxy-methyl-2-furfural; *cis*-3 = *cis*-3-hexen-1-ol; dec ac = decanoic acid; et dec = ethyl decanoate; et hex = ethyl hexanoate; et lac = ethyl lactate; et oct = ethyl octanoate; et van = ethyl vanillin; eug = eugenol; fur = furfural; ger = geraniol; gua ket = guaiacyl ketone; hex ac = hexyl acetate; is ac = isoamyl acetate; lin = linalool; oct ac = octanoic acid; van = vanillin; van der = vanillin derivate; whis *cis* = whiskylactone-*cis*; whis *trans* = whiskylactone-*trans*.

indicated by the clustering procedure for the blending process, but also those considered from distillation in the previous section.

The artificial fruit attribute, accounting for FR1 characteristics, exhibited correlations with hexyl acetate ($r = 0.47$), isoamyl acetate ($r = 0.32$), and higher correlations with ethyl decanoate ($r = 0.84$), ethyl octanoate ($r = 0.85$), and ethyl hexanoate ($r = 0.88$).

The linalool attribute, accounting for FR2 sensory notes, had a correlation coefficient with linalool of $r = 0.48$, whereas geraniol and 1-hexanol showed low correlations, $r = 0.28$ and $r = 0.13$, respectively. Esters, however, which accounted for FR1 sensory notes, also exhibited high correlations with the linalool attribute. These correlations appear in Table 1 and correspond to ethyl decanoate, ethyl octanoate, ethyl hexanoate, hexyl acetate, and isoamyl acetate, with values of $r = 0.71$, $r = 0.7$, $r = 0.74$, $r = 0.48$, and $r = 0.54$, respectively. Figure 3 shows that the artificial fruit attribute was correlated with both linalool and citrus attributes, which explains why the distinction between fractions FR1 and FR2 is no longer obvious in finished products (blended and aged).

The tails attribute, distinctive for FR3 samples, had high correlation with 2-phenylethanol ($r = 0.65$) and ethyl lactate ($r = 0.78$).

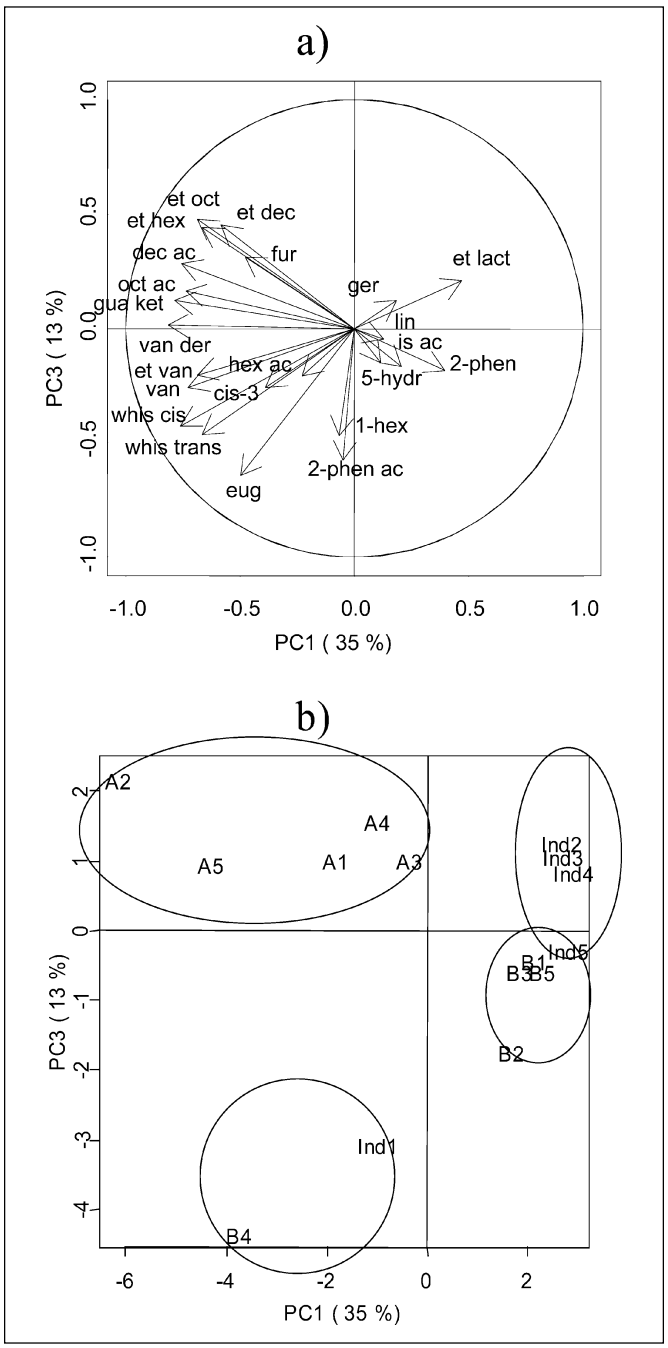

Figure 5—1st and 3rd principal components calculated with chemical compounds of finished Piscos. (a) variable loadings in the correlation circle; (b) sample scores. For abbreviations, see legend of Figure 4.

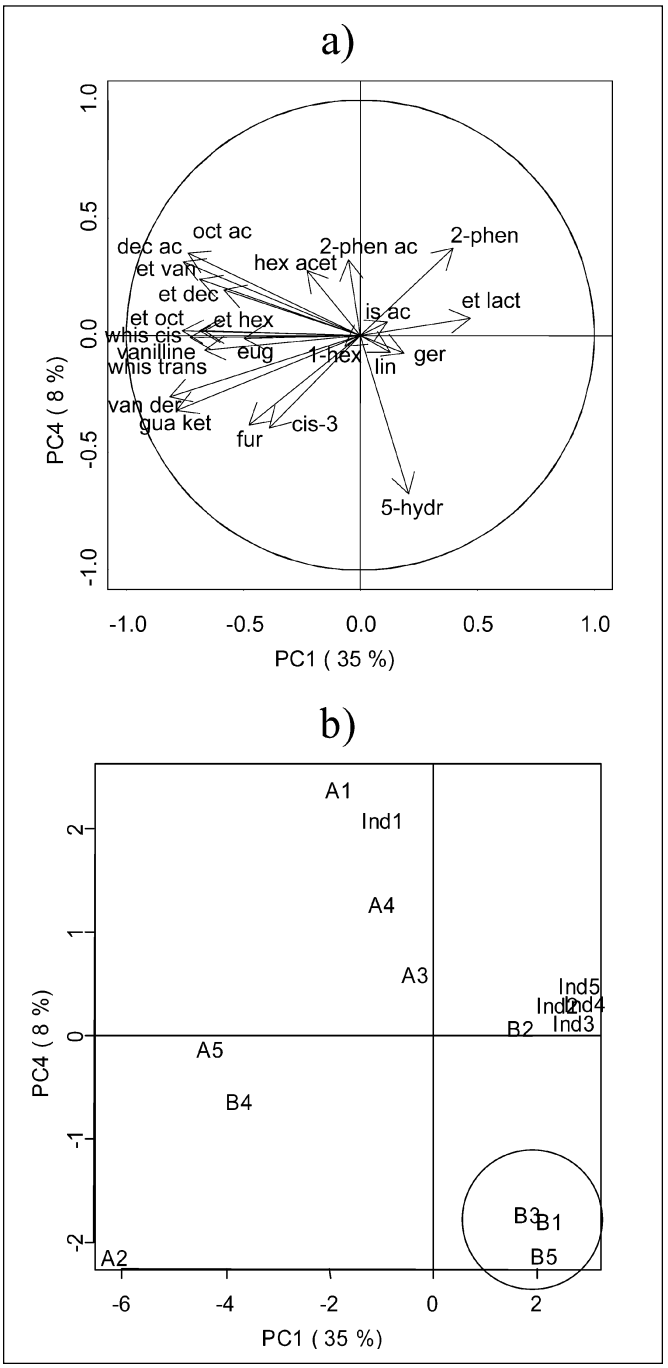

Figure 6—1st and 4th principal components calculated with chemical composition of finished Piscos. (a) variable loadings in the correlation circle; (b) sample scores. For abbreviations, see legend of Figure 4.

Aging

Based on the odor attributes of finished Piscos, PC1 and PC2 showed B1, B3, B4, B5, and IND1 Piscos to have high intensities of oak, vanilla, and caramel attributes (Figure 3). The PC3 axis, based on chemical composition (Figure 5), clustered B4 and IND1 Piscos with high concentrations of eugenol and whisky lactones. Figure 6 shows that PC4 accounts for 5-hydroxy-methyl-2-furfural and that B1, B3, and B5 Piscos had high concentrations of 5-hydroxy-methyl-2-furfural.

Table 1 shows the correlation values between eugenol ($r = 0.8$), whisky lactone *cis* ($r = 0.67$), whisky lactone *trans* ($r = 0.73$) and of 5-hydroxy-methyl-2-furfural ($r = 0.34$) with oak attribute.

Discussion

Molecules exhibiting (1) a high correlation with the distinctive notes of a production stage, (2) agreement between the sensory notes in (1) and their pure molecule odors, and (3) appearance at this specific production stage were selected as chemical markers. Analysis of distillate fractions showed that sensory data and chemical data had similar degrees of complexity, needing just 2 and 3 principal components, respectively. In contrast, the chemical composition of finished products (involving distillation, blending, and aging) proved more complex, requiring 4 principal components to represent more than 80% of the data variance. Their sensory maps, on the other hand, required just 2 principal components. Hence, differences in chemical composition produced in post-fermentation production processes are not directly transferred to the sensory attributes of the products. Finished Pisco could be differentiated using 2 sensory directions: fruity notes (which correlate negatively with chemical notes) and aging notes. This result, however, is common for complex products, in which a large number of odorant molecules are associated with far fewer sensory signals.

Distillation

PCA correlations between volatile molecules and sensory attributes of distillate fractions verify results of previous work obtained with Partial Least Squares analysis (PLS) on exactly the same set of samples (Peña y Lillo and others 2003). The latter work was based in the covariance (basis of PLS calculations) between the sensory and chemical data, whereas the current work is based on the variance (basis of PCA calculations) of each data set. When the 2 sets of data are very similar (as the case of chemical and sensory data of distillate fractions in this work), the 2 techniques should be analogous.

Distillation separates molecules according to volatility. More volatile molecules are distilled earlier in the process than less volatile ones corroborating previous reports for cognac distillates: ethyl esters are distilled in the heads; superior alcohols are distilled in the heart; and phenylethanol, furfural, ethyl lactate, and fatty acids are distilled in the tails (Jouret and others 2000). A recent work determining volatilities in hydroalcoholic solutions (Peña y Lillo and others 2003) explains the separation of molecules during distillation. Esters have the highest partition coefficient followed by linalool and *cis* 3-hexen-1-ol, both appearing in fraction FR2.

Distillation fractioning can be tracked efficiently. Sample clusters obtained from odor intensities were identical to those from chemical compositions.

The FR1-associated molecules (Table 1) are all esters with fruity descriptors. This property is consistent with the "artificial fruit" attribute they correlate with in Piscos. Hexyl acetate is described as fruity, green, pear, apple (IFF 2003); ethyl decanoate as sweet, oily-nut like (Arctander 1994); ethyl octanoate as pineapple (Budavari 1996), fruity-winey, suggestive of apple, banana, pineapple (Arctander 1994); ethyl hexanoate as pineapple (Budavari 1996), fruity-winey, suggestive of apple, banana, pineapple, with a slightly floral undertone (Arctander 1994); and isoamyl acetate as fresh fruit (Arctander 1994). Chemical markers for FR1 were ethyl decanoate, ethyl octanoate, ethyl hexanoate, hexyl acetate, and isoamyl acetate and are set in bold type in Table 1. The sensory note, the process they denote as well as their respective correlations, are also shown.

FR2 had strong linalool notes followed by citrus. The pure molecule odor of linalool is described as sweet, floral, creamy (Wang and others 1994; Ito and others 2002), geraniol as mild and sweet, floral rose-type odor (Arctander 1994); *cis*-3-hexen-1-ol as green grass (Acree and Arn 2003); 1-hexanol as resinous (Acree and Arn 2003). 1-hexanol had the highest correlation with the linalool attribute but an inconsistent pure molecule odor. Linalool and citrus attributes were consistent with the pure molecule odor of linalool and geraniol, but since the latter showed very little correlation with the linalool attribute, only the linalool molecule was considered as a chemical marker (Table 1).

Pure molecule odor of FR3-associated compounds include the following: octanoic acid described as sweaty (Acree and Arn 2003), decanoic acid, rancid (Budavari 1996); furfural as almond (Ribereau-Gayon and others 1998; Acree and Arn 2003); 2-phenylethanol as floral, rose (Budavari 1996); and ethyl lactate as a mild, ethereal buttery odor (Arctander 1994). With respect to their pure molecule odors, all FR3-associated compounds except 2-phenylethanol agreed with the tails attribute. The only molecule presenting a correlation under 0.5 was 2-phenylethanol, whereas furfural had the highest correlation ($r = 0.8$). Chemical markers for fraction FR3 are, therefore, furfural, decanoic acid, octanoic acid, and ethyl lactate (Table 1).

Blending

Finished (blended and aged) products are more complex than distillation samples; differentiation is less evident making tracking more difficult. Even so, many molecules correlating with a distillate fraction following blending show similar trends with those correlating following distillation fractioning.

Unlike for distillation fractioning, here differentiation between FR1- and FR2-associated samples was poor because artificial fruit and citrus attributes were correlated. Sample cluster A1, A3, and A4 exhibited the strongest intensity of artificial fruit attribute and, to a lesser extent, citrus (Figure 3). Molecules correlating with the cluster were hexyl acetate, isoamyl acetate (previously selected as markers for FR1 fractioning), both of which presented low correlations with the artificial fruit attribute (Table 1) and therefore cannot be considered as blending markers. Other markers previously selected for FR1 fractioning were also tested, and revealed high correlation coefficients with artificial fruit attribute, and include ethyl decanoate, ethyl octanoate, and ethyl hexanoate, and hence have been selected as markers for FR1 blending (Table 1).

Samples A2 and A5 exhibited high intensities of FR2-associated attributes linalool and citrus. Molecules correlating with this sample cluster, however, were aging-associated lactones (Figure 4), the FR1 markers (Figure 5)—ethyl hexanoate, ethyl octanoate, ethyl decanoate, and the FR3-associated molecules, octanoic acid and decanoic acid (Figure 5). FR2 cluster matching obtained for distillation fractioning did not happen again with finished products that are more complex. Products with high intensities of FR2-associated attributes did not show high correlations with their respective FR2 fractioning markers. Correlation between the linalool attribute and the markers previously selected for FR2 fractioning was found (Table 1). Linalool, already selected as a marker for FR2 fractioning, showed the highest, although still not a very strong correlation of $r = 0.48$. Selected markers for FR2 blending, set in bold type in Table 1, are ethyl hexanoate, ethyl octanoate, ethyl decanoate, which have fruity-floral attributes, and linalool.

The FR3 cluster of finished products (IND2, IND3, IND4, IND5, and

B2) was similar to the FR3 cluster of distillate fractions showing strong correlations with 2-phenylethanol and ethyl lactate. Both molecules' correlation coefficient with tails attribute was higher than 0.6 and therefore both are markers for FR3 blending. The remaining molecules associated with FR3 fractioning, octanoic acid, decanoic acid, and furfural (which is a marker for FR1 fractioning) had low correlation coefficients with tails notes and are therefore not markers for FR3 blending.

Aging

Sensory data (Figure 3) revealed the highest aging note ratings in IND1 and B4 Piscos followed, to a lesser extent, by B1, B3, and B5. Chemical data (Figure 5) showed IND1 and B4 Piscos to have high concentrations of eugenol and whisky lactones, whereas B1, B3, and B5 had a high concentration of 5-hydroxy-2-methyl-furfural (Figure 6).

Aging in oak casks has been investigated extensively for wines and spirits (Mosedale and Puech 1998; Chatonnet 1999). Volatile phenols (eugenol) result from a breakdown of lignin in the wood during toasting (Chatonnet 1999). Whisky lactones, one of the most abundant volatile compounds in oak wood, are extracted in oak-aged wines and brandies in concentrations depending on the wood variety (Hale and others 1999) and seasoning (Ribereau-Gayon and others 1998).

5-hydroxy-2-methyl-furfural stands out among abundant caramel volatiles (Defaye and others 2000). Caramel is added to many spirits, such as Mezcal of Oaxaca (IRU 1998), tequila (Baja Life Online 2003), rum (AVL 2003), whisky (Broom 2001), as well as brandies (Pons and others 1991; Quesada Granados and others 1996).

Pure molecule odors of all aging-associated molecules agree with oak notes. Eugenol has a spicy clove odor (Francis and others 1992; Ribereau-Gayon and others 1998); whisky lactones (*cis* and *trans*) have woody, coconut notes (Masuda and Nishimura 1971); and 5-hydroxymethyl-2-furfural has caramel notes (Defaye and others 2000). Aging process chemical markers hence are eugenol, whisky lactone *cis*, whisky lactones *trans*, 5-hydroxy-2-methyl-furfural, and appear in bold type in Table 1. The latter aging-associated molecule does not come from oak casks, however, but from either the addition of caramel or caramelization of free sugar during distillation and is therefore presented as a marker for "caramel addition" (Table 1). Markers associated with both oak aging and caramel addition contribute to perceived aging attributes in finished products. The results illustrate the composite nature of oak, caramel and vanilla odor in Pisco samples, which may also apply to other spirits.

Using the current technique, chemical markers selected for fractioning, blending, oak aging or the addition of caramel may also correspond to odor impact molecules. Literature covers some of the chemical markers in FR1 and FR2, which reveals that ethyl hexanoate, ethyl octanoate, isoamyl acetate, and linalool are probable odor impact molecules in Chilean Pisco (Peña y Lillo and others 2003). The study identified probable odor impact molecules upon comparing the odor air threshold with the headspace concentration that was calculated using measured partition coefficients and liquid concentrations.

Conclusions

Chemical markers associated with each stage of production enable producers of Muscat wine distillates to track a product's main odor attribute efficiently throughout post fermentation processes. Our results suggest that just 1 corresponding chemical marker is sufficient for tracking a given production stage. However, validation with additional Pisco samples would indicate to a greater extent the validity of this conclusion.

In the head of the distillate highly volatile molecules appear, such as the esters, ethyl hexanoate, ethyl octanoate, ethyl decanoate, hexyl acetate, and isoamyl acetate, which account for the artificial fruit attribute. Later on, less volatile compounds are distilled in the 1st and 2nd parts of the heart that respectively account for the attributes linalool and tails. The 1st part of the heart can be tracked with the linalool molecule, whereas the 2nd part of the heart can be followed with octanoic and decanoic acids, ethyl lactate, and furfural that account for the tails attribute.

In blended and aged finished products, chemical markers accounting for the effects of distillate fractions were similar but not identical to the markers from samples obtained directly from the purely distilled samples. Chemical markers for the head are ethyl hexanoate, ethyl octanoate, ethyl decanoate. Differentiation between the head and the 1st part of the heart is less evident than in the purely distilled samples due to the linalool and artificial fruit attribute correlation. Chemical markers for the 1st part of the heart, therefore, include linalool and esters ethyl hexanoate, ethyl octanoate, and ethyl decanoate. The blending of the 2nd part of the heart can be tracked with chemical markers 2-phenylethanol, ethyl lactate, and decanoic acid.

Oak attribute results mainly from aging in oak casks and may be tracked with eugenol and whisky lactones. However, caramel addition also contributes to oak attribute and can be tracked with 5 hydroxy-methyl-2-furfural.

Results of the multivariable clustering technique applied here to Muscat wine distillates may prove useful for other distillates sharing the processes in the production of Pisco: distillation fractioning, blending, oak aging, and the addition of caramel.

This work provides a viable approach for tracking the sensory contribution of any food-production process. Using chemical markers to follow the main sensory feature of a process would bring a series of consumer-oriented benefits to the production line such as rapid feedback for a controlled process, sensory quality improvement, or the early detection of defects.

Acknowledgments

This work was supported by project ECOS-CONICYT C00B08. Marcial Peña y Lillo is indebted to the Fellowship Program from Consejo Nacional de Ciencia y Tecnología (CONICYT) in Chile and to the French government while in France for financial support. We thank Ricardo Perez for his valuable comments, Nicolas Bonnaire and Loreto Valenzuela for their technical assistance in the chemical identification of samples, and Alex Crawford for editorial assistance.

References

[AVL] A-1 Virtual Liquor.com. 2003. Rum. Available from: http://www.geocities.com/shoppmom/rum.html. Accessed Nov 10, 2003.
Acree T, Arn H. 2003. Flavornet lexicon. Datu Inc. Available from: http://www.flavornet.org. Accessed Aug 12, 2004.
Agosin E, Belancic A, Ibacache A, Baumes R, Crawford A, Bayonove C. 2000. Aromatic potential of certain Muscat grape varieties important for Pisco production in Chile. Am J Enol Vitic 51(4):404–8.
Arctander S. 1994. Perfume and flavor chemicals (aroma chemicals). Carol Stream, Ill.: Allured Publishing.
Arrhenius SP, McCloskey LP, Sylvan M. 1996. Chemical markers for aroma of Vitis vinifera Var. Chardonnay regional wines. J Agric Food Chem 44(4):1085–90.
[BLO] Baja Life Online. 2003. Baja Sur Tequila and Mariachi Festival. Available from: http://www.vivatequila.com/tequila/glossary.html. Accessed Nov 10, 2003.
Baumes R, Bayonove C, Gunata Z. 1994. Connaissances actuelles sur le potentiel aromatique des muscats. Progres Agric et Vitic 111(11):251–6.
Bayonove C, Baumes R, Crouzet J, Günata Z. 2000. Aromes. In: Flanzy C, editor. Enologie: fondements scientifiques et technologiques. Paris: Technique et Documentation.
Bayonove C, Cordonnier R. 1971. Rècherches sur l'arôme du muscat. Ann Technol Agric 20:347–50.
Belancic A, Agosin E, Ibacache A, Bordeu E, Baumes R, Razungles A, Bayonove C. 1997. Influence of sun exposure on the aromatic composition of Chilean Muscat grape cultivars Moscatel de Alejandria and Moscatel rosada. Am J Enol Vitic 48(2):181–6.
Bordeu E, Formas G, Agosin E. 2004. Proposal for a standardized set of sensory terms for pisco, a young, Muscat wine distillate. Am J Enol Vitic 55(1):104–7.
Broom D. 2001. Caramel addition may prove sticky issue for Scotch's marketeers. Available from: http://just-drinks.com/features_detail.asp?art = 501&lk = nd02. Accessed Nov 10, 2003.
Budavari S, editor. 1996. The Merck index. Whitehouse Station, N.J.: Merck and Co.
Chatonnet P. 1999. Discrimination and control of toasting intensity and quality of oak barrels. Am J Enol Vitic 50(4):479–93.

Defaye J, Garcia Fernandez JM, Ratsimba V. 2000. Les molécules de la caramélisation : structure et méthodologies de détection et d'évaluation. L'actualité Chim 11:24–7.
Etiévant P. 1991. Wine. In: Maarse H, editor. Volatile compounds in foods and beverages. New York. p 483-536.
Francis IL, Sefton MA, Williams PJ. 1992. A study by sensory descriptive analysis of the effects of oak origin, seasoning, and heating on the aromas of oak model wine extracts. Am J Enol Vitic 43(1):23–30.
Gunata Z, Bayonove C, Baumes R, Cordonnier R. 1985. The aroma of grapes. I. Extraction and determination of free and bound fractions of some grape aroma components. J Chromatogr 331(1):83–90.
Hale M, McCafferty K, Larmie E, Newton J, Swan J. 1999. The influence of oak seasoning and toasting parameters on the composition and quality of wine. Am J Enol Vitic 50(4):495–502.
Herraiz M, Reglero G, Herraiz T, Loyola E. 1990. Analysis of wine distillates made from Muscat grapes (Pisco) by multidimensional gas chromatography and mass spectrometry. J Agric Food Chem 38(7):1540–3.
[IFF] Intl. Flavor & Fragrances Inc. 2003. Available from: http://www.iff.com. Accessed Nov 10, 2003.
IRU Inc. 1998. Mezcal of Oaxaca. Available from: http://www.viprofix.com/iru/mezcal.html. Accessed Nov 10, 2003.
Ito Y, Sugimoto A, Kakuda T, Kubota K. 2002. Identification of potent odorants in Chinese jasmine green tea scented with flowers of *Jasminum sambac*. J Agric Food Chem 50(17):4878–84.
Jeurings HJ, Kuppers FJEM. 1980. High performance liquid chromatography of furfural and hydroxymethylfurfural in spirits and honey. J Assoc Off Anal Chem 63(6):1215–8.
Jouret C, Cantagrel R, Galy B. 2000. Eaux de vie d'origine viticole. In: Flanzy C, editor. Enologie: fondements scientifiques et technologiques. Paris: Technique et Documentation.
Kotseridis Y, Baumes R. 2000. Identification of impact odorants in Bordeux red grape juice, in the commercial yeast used for its fermentation, and in the produced wine. J Agric Food Chem 48(2):400–6.
Lambrechts MG, Pretorius IS. 2000. Yeast and its importance to wine aroma: a review. S Afr J Enol Vitic 21:97–129.
Marais J. 1983. Terpenes in the aroma of grapes and wines: a review. S Afr J Enol Vitic 4(2):49–58.
Masuda M, Nishimura K. 1971. Presence and significance of two diastereomers of 4-methyl-gamma-octalactone in aged distilled liquors. Phytochemistry 10(6):1401–2.
Mosedale JR, Puech JL. 1998. Wood maturation of distilled beverages. Trends Food Sci Technol 9(3):95–101.
Peña y Lillo M, Agosin E, Athès V, Bordeu E, Casaubon G, Latrille E, Martin N, Pérez-Correa R, Souchon I. 2003. Relation between odour perception and physico-chemical properties of volatile compounds in Chilean Pisco spirit. In: Le Quéré JL, Etiévant P, editors. Flavour research at the dawn of the Twenty-first Century. Cachan, France: Lavoisier. p 686–9.
Peña y Lillo M, Latrille E, Casaubon G, Agosin E, Bordeu E, Martin N. 2005. Comparison between odour and aroma profiles of Chilean Pisco spirit. Food Qual Pref. 16(1):59–70.
Pons I, Garrault C, Jaubert JN, Morel J. 1991. Analysis of aromatic caramel. Food Chem 39(3):311–20.
Quesada Granados J, Villalon Mir M, Lopez Garcia-Serrana H, Lopez Martinez MC. 1996. Influence of aging factors on the furanic aldehyde contents of matured brandies: aging markers. J Agric Food Chem 44(6):1378–81.
SAS Inst. 1990. User's guide: statistics. Version 6 Edition. Cary, N.C.: SAS Inst.
Reynolds AG, Wardle DA, Dever M. 1993. Terpene response to pressing, harvest date, and skin contact in vitis vinifera. HortScience 28(9):920–4.
Ribereau-Gayon P, Glories Y, Maujean A, Dubourdieu D. 1998. Traité d'oenologie. Paris: Dunod.
Schreier P. 1979. Flavour composition of wines: a review. CRC Crit Rev Food Sci Nutr 11:59–111.
Valenzuela L. 2002. Politica de destilacion y calidad aromatica del destilado (Pisco) [MSci thesis]. Catholic Univ. of Chile. Available from: Catholic Univ. of Chile Library, Santiago, Chile.
Wang D, Ando K, Morita K, Kubota K, Kobayashi A. 1994. Optical isomer of linalool and linalool oxides in tea aroma. Biosci Biotechnol Biochem 58(11):2050–3.

Appendix

Gas chromatography-mass spectrometry (GC-MS) identification and quantification of volatile compounds in Pisco samples Distillate fractions and finished Piscos were analyzed identically, by means of GC-MS; 15 volatile compounds were identified in distillate fractions and were also quantified by using 4-nonanol as internal standard in distillate fractions and finished samples (Table A1).

Table A1—Volatile compound quantification of Pisco samples (mg/L)

	Compounds (mg/L)														
Sample	Hexanol	2-Phenylethanol	*cis*-3-hexen-1-ol	Octanoic acid	Decanoic acid	Isoamyl acetate	Ethyl hexanoate	Ethyl lactate	Ethyl octanoate	Ethyl decanoate	Hexyl acetate	2-Phenylethyl acetate	Linalool	Geraniol	Furfural
A1	4.471	2.144	0.309	7.363	8.886	3.207	1.686	2.276	4.595	12.701	0.468	0.488	3.637	0.081	1.277
A2	3.287	0.678	0.343	8.760	7.440	0.654	1.818	0.762	5.377	8.711	0	0	0.233	0.105	4.577
A3	4.313	1.084	0.331	6.493	5.715	2.342	1.379	6.909	3.802	7.721	0.215	0.309	2.045	0.182	1.126
A4	3.940	1.444	0.260	5.413	6.252	2.409	1.597	1.805	4.550	11.753	0.215	0.325	3.575	0.241	1.327
A5	3.811	1.632	0.329	6.903	7.126	0.696	1.427	3.028	4.328	9.353	0.057	0	0.169	0.083	2.412
B1	4.246	0.980	0.331	3.083	2.156	2.663	0.810	31.764	1.756	3.641	0.161	0.303	3.394	0.162	1.605
B2	5.337	7.308	0.378	4.506	3.186	1.146	0.422	27.093	0.917	1.805	0.134	0.386	1.178	0.125	0.168
B3	4.441	1.284	0.330	2.972	2.106	3.025	0.879	32.973	1.843	3.772	0.165	0.333	3.338	0.150	1.646
B4	4.699	5.050	0.380	5.301	3.991	1.646	0.651	24.800	1.456	2.991	0.269	0.422	1.834	0.124	2.105
B5	4.374	1.164	0.331	3.243	2.304	2.895	0.826	31.873	1.770	3.710	0.157	0.311	3.516	0.167	1.640
Ind1	3.719	16.764	0.240	7.616	4.388	2.390	0.597	23.610	0.933	1.701	0.105	0.662	1.095	0.110	1.496
Ind2	2.754	14.393	0.242	5.106	2.277	0.945	0.415	346.703	0.758	1.151	0	0.022	0	0.059	2.535
Ind3	2.344	6.348	0.168	3.538	2.018	1.346	0.391	118.861	0.831	1.901	0	0	2.617	0.337	1.369
Ind4	3.110	17.738	0.294	5.052	2.255	1.258	0.453	344.946	0.835	2.060	0	0.173	0	0.080	2.246
Ind5	4.561	23.190	0.195	3.333	1.407	0.381	0.280	52.881	0.348	0.398	0	0.028	0.051	0.078	1.822
FR1	1.840	3.696	1.304	2.304	0	261.886	24.959	2.174	63.957	16.090	5.095	0.068	4.755	0	1.448
2.338	2.374	0	1.347	0	331.366	27.536	1.342	78.189	18.574	5.519	0.148	5.620	0	0.911	
1.440	0	0.167	1.880	0	274.263	25.231	0.791	56.983	14.086	3.162	0	3.241	0	0.549	
1.867	0	0	1.371	0	294.827	30.966	0.419	80.397	29.371	5.612	0.048	4.153	0	3.219	
0.818	1.362	0	1.903	0	247.440	20.139	1.144	39.861	5.848	2.303	0	1.095	0	1.246	
FR2	1.831	0.115	1.323	1.438	0	15.269	2.390	2.644	6.672	2.497	0.564	0.315	3.705	0.490	0.860
2.011	3.665	2.403	3.005	1.385	10.398	1.940	2.471	6.425	2.159	0.453	0.646	3.961	0.781	1.132	
2.017	7.236	2.033	4.664	3.143	16.196	1.515	2.080	6.216	1.551	0.233	1.000	3.073	0.917	1.367	
2.350	2.118	2.795	2.327	0	14.070	3.080	2.337	8.452	2.677	0.521	0.494	4.483	0.752	1.265	
FR3	1.114	0	2.012	1.586	0	0	0	2.879	2.593	0.686	0	0.417	1.233	0	1.788
0.296	1.878	0	3.982	0	0	0	1.745	2.804	0.816	0	0.441	0.673	0	2.774	
0	7.027	2.234	5.440	4.521	0	0.432	5.485	4.920	1.223	0	0.696	0.880	0	3.162	
0.458	9.042	1.713	7.868	4.749	0	0	3.946	4.614	1.054	0	0.946	0.778	0.665	5.071	
0.699	0.212	1.944	2.810	3.349	0	0	2.648	4.253	1.333	0	0.599	0.863	0	2.956	

[a]Eight further compounds, typically associated with oak aging of wines and distillates, were identified in finished Piscos (Table A2). Distillate fractions did not present these molecules. Volatile quantification was not done and hence data are expressed in chromatographic areas, which allows the comparison among samples for a given molecule but not among different molecules.

Table A2—Identification of aging associated molecules[a,b]

	Compounds (chromatographic areas)							
Sample	Whisky lactone trans	Whisky lactone cis	Eugenol	Vanillin	Ethyl vanillin	Vanillin derivate	Guaiacyl ketone	5-Hydroxymethyl 2-furfural
A1	0	5.084	0	13.252	2.530	1.756	0.762	3.368
A2	3.714	22.472	1.048	34.425	4.694	19.338	8.045	15.280
A3	0	1.978	0	8.542	1.696	1.709	1.309	9.206
A4	0	7.498	0	20.177	3.608	1.781	1.019	1.913
A5	4.017	18.370	0	80.497	6.472	7.415	3.555	4.251
B1	0.420	0	0	9.719	0	0	0	54.319
B2	0.892	3.362	0	10.670	1.673	0.704	0.281	12.067
B3	0	0	0	8.980	0.994	0	0.573	55.539
B4	5.890	35.556	2.990	56.135	6.347	10.286	3.984	11.491
B5	0.235	0	0	10.814	0	0	0	70.312
Ind1	4.323	22.131	1.682	39.649	5.102	3.739	0	4.808
Ind2	0	0	0	5.094	2.134	0	0	1.684
Ind3	1.491	2.589	0	6.982	3.299	0.751	0	0
Ind4	0	0	0	1.731	0	0	0	0
Ind5	0	0	0	6.062	3.489	0	1.113	0
FR1	0	0	0	0	0	0	0	0
FR1	0	0	0	0	0	0	0	0
FR1	0	0	0	0	0	0	0	0
FR1	0	0	0	0	0	0	0	0
FR1	0	0	0	0	0	0	0	0
FR2	0	0	0	0	0	0	0	0
FR2	0	0	0	0	0	0	0	0
FR2	0	0	0	0	0	0	0	0
FR2	0	0	0	0	0	0	0	0
FR3	0	0	0	0	0	0	0	0
FR3	0	0	0	0	0	0	0	0
FR3	0	0	0	0	0	0	0	0
FR3	0	0	0	0	0	0	0	0
FR3	0	0	0	0	0	0	0	0

[a]Odor profiling of Pisco samples.
[b]Distillate fractions and finished Piscos odor characteristics were assessed by descriptive analysis. The mean intensity for each discriminant attribute and each sample appear below (Table A3).

Table A3—Odor attributes mean intensities of Pisco samples (mg/L).

Sample	Acetal-dehyde	Tails	Acetic acid	Ethyl acetate	Oak	Caramel	Vanilla	Raisins	Citric	Artificial fruit	Linalol	Hay
A1	1.33	1.17	1.58	2.33	2.00	2.00	1.50	2.25	2.25	2.17	2.08	0.50
A2	1.08	1.58	1.25	2.08	2.83	1.75	1.75	1.83	2.83	2.00	2.08	0.75
A3	1.25	0.67	0.83	2.33	2.25	1.17	1.50	2.08	1.75	1.67	2.67	0.50
A4	1.19	0.78	1.25	1.81	1.72	1.72	1.69	1.81	2.58	1.97	3.03	0.36
A5	1.17	0.83	1.22	1.97	2.78	2.08	2.08	2.11	2.53	1.36	2.36	0.56
B1	2.25	0.92	1.58	2.58	2.75	1.92	1.92	2.33	1.67	1.00	1.75	1.42
B2	2.67	2.33	2.25	3.08	2.58	1.50	1.58	2.33	2.25	0.50	1.33	1.33
B3	1.58	1.25	1.75	2.42	2.83	2.00	2.00	2.50	2.67	1.42	2.17	1.42
B4	1.58	1.17	1.42	1.94	4.28	2.36	2.28	2.25	1.64	1.03	1.83	1.11
B5	1.97	1.64	1.83	2.03	3.28	2.28	1.94	2.14	2.03	1.19	2.11	1.19
Ind1	1.44	0.92	1.00	1.81	3.47	2.33	2.11	2.28	2.22	1.00	2.39	1.00
Ind2	3.31	2.42	2.64	3.28	2.11	1.31	0.67	2.06	1.86	1.47	1.36	1.78
Ind3	2.50	1.92	2.42	2.58	2.17	1.75	1.33	2.75	1.50	0.50	1.42	1.83
Ind4	4.00	3.92	2.92	4.00	2.67	1.75	1.08	1.50	1.42	0.83	0.92	2.00
Ind5	3.00	2.42	2.33	2.83	2.33	1.67	1.08	1.75	1.42	0.83	0.75	1.58
FR1	1.75	1.25	2.17	3.42	1.00	1.42	1.33	1.17	2.50	5.25	2.58	0.42
	1.67	0.67	1.25	3.08	0.50	1.25	1.17	1.00	2.50	4.58	2.83	0.58
	1.39	0.69	1.58	2.81	0.97	1.33	1.33	1.50	2.67	4.94	3.00	0.58
	1.17	0.92	2.08	2.83	1.08	1.42	1.67	1.42	2.83	5.33	3.17	0.75
	2.17	0.92	2.00	3.58	1.17	1.58	1.92	1.58	2.25	3.92	2.83	0.92
FR2	1.00	0.67	1.08	2.25	1.58	1.83	1.33	1.75	3.00	2.00	3.50	0.25
	1.39	0.92	1.44	2.00	1.53	1.69	1.33	1.83	2.42	2.42	2.94	0.58
	0.75	1.33	1.58	1.75	1.75	1.08	1.58	1.92	3.17	2.17	2.67	0.83
	1.25	1.28	1.39	1.69	1.64	1.86	1.86	1.69	2.86	2.19	3.00	0.78
FR3	1.94	2.72	2.17	2.14	1.64	1.69	1.11	2.03	1.83	1.22	1.64	1.69
	3.33	5.00	2.33	3.67	1.67	0.92	0.75	1.67	1.17	1.17	1.17	3.00
	2.50	3.75	2.08	2.50	2.42	1.42	1.25	1.92	1.67	0.92	1.17	1.50
	2.83	5.17	2.33	2.67	1.58	0.83	0.25	1.58	0.67	0.33	0.33	1.75
	3.42	4.75	2.42	3.00	1.67	0.58	0.75	2.08	1.42	0.92	1.33	2.33