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Comparison between odour and aroma profiles of Chilean Pisco spirit

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Abstract

Precise sensory measurements of odour (orthonasal) and aroma (retronasal olfactory perception) are time and resource consuming. The aim of this work was to develop improved olfactory tasting procedures. Odour and aroma profiles of 13 Pisco spirits and 14 distillation fractions were obtained through descriptive analysis by a panel of 12 trained subjects. The samples were discriminated by 12 odour and 11 aroma attributes out of 13, with odour being slightly more discriminant at a panel and individual level. Samples were differentiated according to the type of distillation fraction and maturation process. None of the tasting modes induced significantly higher intensity judgement, with the exception of linalol whose average sample odour intensity was higher. However, there were differences in intensity scores between modes due to subject-mode interactions for all attributes except linalol and, to a lesser extent, to product-mode interactions for tails, ethyl acetate and linalol. Partial least square (PLS) models gave a good prediction of aroma from odour scores, except for oak attribute which exhibited a non-linear behaviour. Overall, Pisco olfactory perception can be limited to odour assessment.

Keywords: Pisco spirits; Alcoholic beverage; Distillation fraction; Descriptive analysis; PLS; Prediction

1. Introduction

Accurate sensory measurements are key tasks for the alcoholic beverage industry. Sensory measurements of both odour (orthonasal perception) and aroma (organoleptic attribute perceptible by the olfactory organ via the back of the nose, i.e. retronasal olfactory perception when tasting (NF ISO 5492, 1995)) are time and resource consuming and also quite tiring for the subjects since a great number of olfactory notes can be elicited by a single product. Besides, Zamora and Guirao (2002) have shown that subjects showed a poor ability to describe Chardonnay Wines using olfactory attributes. They rather tend to select terms expressing gustatory or trigeminal sensations (sweet, sour, bitter, prickling, body, astringency). As odour and aroma seem quite difficult to assess, it is of great interest for the sensory analyst to understand the possible difference between odour and aroma perceptions in order to optimise the tasting protocols and limit subject fatigue especially when assessing high alcohol content beverages, for which their strength causes carry over problems for in-mouth evaluation.

A key task in the olfactory profiling of a distilled beverage is the selection and learning process of a reduced set of descriptive terms. The latter was shown to improve assessor's performance in odour assessment of several distillates such as pear acquavite, grappa, white rum, vodka, gin and white tequilas (McDonnell, Hulin-Bertaud, Sheehan, & Delahunty, 2001), to lead to successful descriptive sensory analysis of whisky odour and flavour (Piggott & Jardine, 1979), and also aroma differentiation of Portuguese brandies with different maturation procedures (Caldeira, Belchior, Climaco, & de Sousa, 2002). Reference sensory standards are of great use in the training process of sensory attributes and have been proposed for a whisky flavour wheel (Lee, Paterson, Piggott, & Richardson, 2001a), and a

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brandy aroma wheel (Jolly & Hattingh, 2001). Inclusion of sensory standards in the training process was shown to allow good discrimination and classification of odours and flavours in whisky (Lee, Paterson, Piggott, & Richardson, 2001b).

Chilean Pisco spirit is by far the most consumed distillate in Chile and Peru. It is obtained by batch distillation, by vapourising Muscat wine in a re-boiler, condensing the vapours, which are partially returned to the alambic while collecting the rest of them into a series of fractions, i.e., distillate fractions, as explained by Leauté (1990) for batch distillation process and for the double distillation process of Cognac in France. Finally, the distillate fractions are blended together with different proportions. The finalisation of the product may also include maturation in oak casks or oak chips and caramel addition. The commercial product is basically composed of ethanol (between 30% and 50% v/v), water and aroma compounds (Agosin, Belancic, Ibacache, Baumes, Crawford & Bayonove, 2003; Herraiz, Reglero, Herraiz, & Loyola, 1990), with the presence of terpenes as a distinctive characteristic. A recent work (Peña y Lillo et al., 2003) has identified some terpenes (linalol, *cis* 3 hexen-1-ol, nerol) and esters (ethyl octanoate, ethyl hexanoate, isoamyl acetate) as potent odorants in Pisco. A standardised vocabulary has been recently set up to describe the Pisco flavour (Bordeu, Formas, & Agosin, in press), but no sensory profile has been reported yet for this specific beverage.

Several psychophysical studies using model solutions including a single odorant in simple solvents have dealt with retronasal and orthonasal olfactory perceptions. Although these two olfactory perception modes stimulate the same sensory receptors in the epithelium, several differences between them have been pointed out. Burdach, Köster, and Kroeze (1985) have shown interindividual differences in the olfactory detection ability between both modes together with intra-individual variations with time. Vapour phase has been reported to be delivered less efficiently by the retronasal route than by the orthonasal route (Pierce & Halpern, 1996), resulting in poorer identification abilities. Voirol and Daget (1986) have shown that perception intensity depends on the absolute quantity of odorant reaching the olfactory epithelium, which corresponds to the difference in the air flow between sniffing (orthonasal) and inhaling (retronasal) the vapour phase, inducing higher intensity judgement for the orthonasal mode. In contrast, they showed that when sipping the odorant, the air flow reaching the epithelium was even smaller than the two vapour phase inputs, but the perceived intensity was higher, indicating that stirring and heating occurring in mouth should help increase perception. Burdach and Doty (1987) reported that retronasal olfactory perception results from a highly dynamic process. Mouth movements increase the air flow driving the food volatile compounds from the oral cavity to the olfactory receptors and therefore enhance olfactory perception.

Interactions between olfactory, gustatory and trigeminal perceptions also seem to play a major role. Suppression of retronasal perception by gustation was reported in the presence of taste-active compounds (Burdach, Kroeze, & Köster, 1984), and also in the presence of trigeminal-active compounds (Green, 1996).

A beverage such as Pisco elicits a variety of olfactory perceptions resulting from a complex mixture of volatile components in a hydro-alcoholic solution. Odour and aroma profiles have been rarely compared in real foods or beverages, and no insight has been given into the relation between the orthonasal and retronasal perception in distilled beverages. To our knowledge, only Aubry, Etiévant, Sauvageot, and Issanchou (1999a) and Aubry, Schlich, Issanchou, and Etiévant (1999b) have carried out such a comparison on a complex product, red Burgundy wine. Their major findings were that both tasting modes presented similar correlations between variables, both served similarly to classify wines according to the winery and both, panel discrimination and repeatability, were slightly better for odour perception. Differences between the two modes were much more influenced by subjects than by product effects.

In the present study, odour and aroma profiles of 29 Pisco spirits were obtained through independently performed descriptive analysis using the same 13 attributes. Our objectives were (1) to validate the use of the Pisco Flavour Wheel for the discrimination of Piscos and distillation fractions used in their blending; (2) to gain a better knowledge of possible individual and panel differences between two tasting modes (orthonasal and retronasal olfactory perception) applied to a complex product; (3) to compare odour and aroma profiles of the products in order to assess the possibility of accurately predicting the product aroma profile from the odour profile, thus shortening the evaluation to the latter tasting mode. Such sensory prediction has not been developed yet and constitutes an original approach to this problem.

2. Materials and methods

2.1. Samples

Twenty-nine products were subjected to sensory evaluation. Fifteen commercially available Chilean Piscos were provided by two major distilleries, named A and B, and by smaller, independent distilleries, subsequently named IND. The amount of new casks and duration of the maturation process depend on the distillery and the Pisco. All commercial Piscos used in the present study were submitted to a maturation process. Piscos A were subjected to the most intense maturation process, i.e., maturation in new casks from 6 months to 2 years; Piscos B to 6 months in new casks and Piscos IND to 3 years in used casks.

Moreover, as Chilean Pisco is a blend of different distillation fractions, 14 distillation fractions (non-commercial products) were included in this study aiming at covering the whole spectra of Pisco samples, and at better understanding the product discrimination. Distillation fractions were obtained from five different distillation runs in an industrial site. In each run, samples were collected at different distillation times, to obtain the "head", or first distillate (FR1), the first part of the "heart" (FR2), and the second part of the "heart" (FR3), coming close to the "tail", towards the end of distillation.

Commercial Piscos and distillation fractions were diluted with water to 20% (v/v) ethanol, coded with 3-digit random numbers and presented in tulip-shaped blue-coloured wine tasting glasses (30 ml per glass) covered with a Petri-dish top. These conditions enabled (1) to standardise the alcoholic content of the different products; (2) to limit the sensory fatigue due to ethanol; (3) to avoid any impact of colour difference on the assessment of the olfactory perceptions and (4) to maximise the accuracy of odour and aroma assessments.

2.2. Subjects

Four women and eight men (aged 24–38 years old, mean age 29 years) from the Catholic University of Chile participated in the study. All subjects were Pisco consumers, eight of them had no previous experience in sensory analysis, and three subjects were enologists (two professionals and one student).

2.3. Procedure

The subjects agreed on a common vocabulary of 13 attributes of the Pisco Wheel (Bordeu et al., in press). They were trained in the good use of the vocabulary by smelling the standards defined for the Pisco Wheel (Table 1) and familiarised with the structured 8-category intensity scale (0 denoting an absence of the considered perception and 7 denoting a very intense perception) during 24 sessions.

Odour (orthonasal perception obtained by sniffing the samples) and aroma (retronasal perception obtained by sipping the samples) sensory profiling were performed in separate sessions. The first nine sessions were dedicated to the assessment of the sample aroma. The following three sessions dealt with odour training aiming at familiarisation with odour intensities. The remaining eight sessions were dedicated to the assessment of the sample odour. Six samples were tested per session and presented in a randomised order to the subjects (commercial Piscos and distillation fractions were distributed homogeneously over all the sessions). Ten of the 29 products were replicated three times to assess panel and subject performance. For in-mouth evaluation, subjects sipped the product and were required to expectorate it after determining the intensities of the attributes. Spring water and soda biscuits were provided to the subjects for rinsing their mouth between samples.

Table 1
Standards from the Pisco Sensory Wheel used for training the panel

Standard	Content in 200 ml of 20% hydroalcoholic solution
Acetaldehyde	10 drops of acetaldehyde, Fluka™
Tails[a]	200 ml of Pisco distillation tails, Capel™
Acetic acid	2 drops of acetic acid, Merck™
Ethyl acetate	2 drops of ethyl acetate, Fisher Scientific™
Oak	10 Chips of French oak, World Cooperage™
Caramel	50 g of cooked brown sugar, Wasil™
Vanilla	1 drop of vanilla essence, H&R™
Raisins	30 re-hydrated raisins (sultanas)
Citrus	5 drops of S-(-)-ß-citronellol, Sigma™
Pear	15 ml pear liquor, Williams Christ™
Artificial fruit	100 ml artificial fruit juice, Yupi™
Linalol	2 drops of linalol, Sigma™
Hay	2 g of soaked hay

[a] Standard not prepared with ethanol.

2.4. Data analysis

A principal component analysis (PCA) was performed on odour and aroma data separately. Within each tasting mode, scores were averaged over subjects and replicates. These analyses aimed at comparing the attribute correlation and sample clustering for each sensory mode. In both cases, principal components were constructed using the covariance matrix (from centred data) since the scales for each attribute were identical.

Data from odour and aroma profiles were analysed separately with a two-factor analysis of variance (ANOVA [1]) (product, subject as random factor) with interaction. The effect of the tasting mode was studied with a three-factor ANOVA [2] (tasting mode, product, subject as random factor) with interactions, on the joint data from odour and aroma. A complementary analysis was made to study the tasting mode effects by subtracting aroma scores from odour scores. The data were analysed with a two-factor ANOVA [3] (product, subject as random factor) with interaction. Individual performance was studied by one-factor ANOVA [4] (product) per subject. When significant differences in ANOVA ($P < 0.05$) were detected, Student–Newman–Keuls multiple comparison test (SNK) was applied to get further detail on factor level difference.

The linear relationship between odour and aroma judgements was investigated by calculating the correlation coefficients (r) between attributes after averaging the scores over subjects and replications.

In order to test the feasibility of predicting aroma profiles from odour profiles, averaged odour data over subjects and replications as X block (predictors) and averaged aroma data as the predicted variable were used in a partial least square regression model (PLS). PLS constructs latent variables or PLS factors by maximising the covariance between an input data set (X block) and the output data set (Y block). Subsequent PLS factors are constructed under the same principle of maximisation, but orthogonal to the previous factors. Finally, multiple linear regression of Y block is obtained with the X block. In this work, single response partial least square regression model (PLS1) was used. There was only one X block containing all odour attributes and 12 Y blocks, each with one aroma attribute to be predicted. PLS1 was chosen instead of multiple response partial least square regression (PLS2) since PLS1 gives a better prediction ability (Lee, Luna-Guzmán, Chang, Barrett, & Guinard, 1999). Only discriminant attributes (from ANOVA [1]) were considered for modelling. PLS factors were obtained using the covariance matrix from the centred data. FR1, FR2 and FR3 samples were used as learning set and A, B and IND Piscos were used for external validation as test set. External validation was chosen instead of internal validation techniques (such as cross-validation) since the former gives more trustful predictive results (Sundberg, 2000). The dimension of the model, which determines the number of PLS factors, was chosen by minimising the squared prediction error (PRESS) calculated by applying the model obtained with the learning set to the test set. Prediction performance for each aroma attribute was calculated by dividing the squared sum of prediction errors (PRESS) by the variance of the mean of the attribute scores ($\mathrm{VAR}_{\mathrm{attribute}}$) where (1) $\mathrm{VAR}_{\mathrm{attribute}} = \frac{\sum_{\mathrm{product}=1,n_p} \mathrm{Variance}_{\mathrm{product}}}{n_p}$, with n_p the number of products, and (2) $\mathrm{Variance}_{\mathrm{product}} = \frac{\mathrm{Variance}_{\mathrm{individual\ scores}}}{n}$, with n being the number of times that the product is evaluated ($n = 36$ for replicated products and $n = 12$ for non-replicated products). In addition, another PLS model was tested for predicting oak aroma attribute. In this case, only Piscos A, B and IND were considered, and the number of PLS factors was determined by minimising the squared prediction error (PRESS) calculated by a leave-one-out cross-validation procedure (Tennenhaus, 1998).

ANOVA and associated multiple comparison tests were performed using SAS software package (SAS®, 1990). PCA and PLS were performed using R 1.2.2 for Windows and by using PLS functions developed by Durand, Roman, and Vivien (1998). Smooth values of Fig. 6 were obtained by the "lowess" function of R 1.2.2 (available at http://perso.club-internet.fr/jf.durand).

3. Results

3.1. Product orthonasal and retronasal properties

Two-factor ANOVA [1] showed a significant product effect for all odour attributes except pear ($P = 0.40$) and all aroma attributes except caramel ($P = 0.22$) and ethyl acetate ($P = 0.09$) attributes. PCA was applied to odour and aroma data separately, considering discriminant attributes from ANOVA [1] plus one aroma attribute (ethyl acetate) whose probability was close to significance ($P < 0.1$). Correlation between sensory attributes in each mode proved to be extremely high. The first two principal components covered 86% of the total variance for odour and 80% for aroma, giving practically the same amount of information in both cases. Attribute loadings on the first two principal components were extremely similar for odour and aroma profiles (Figs. 1a and 2a, respectively), indicating similar attribute correlation. The first principal component (PC1) differentiated products with fruity and terpenic notes (linalol,

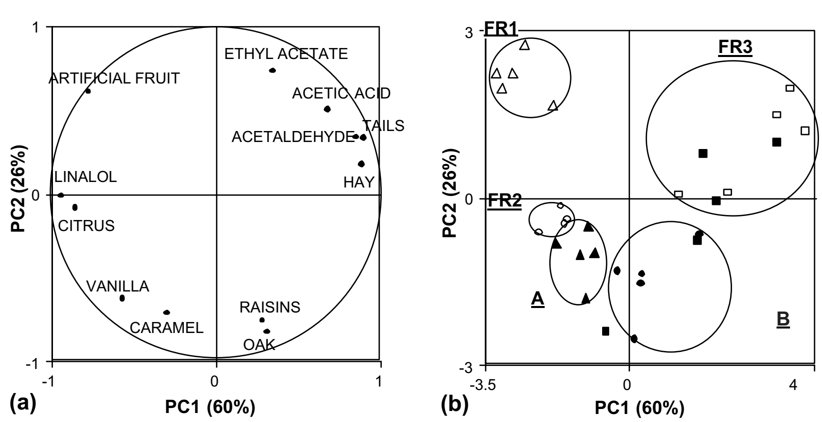

Fig. 1. First two principal components of PCA on odour sensory scores. (a) Attribute loadings, (b) sample plot including distillate fractions FR1 (Δ), FR2 (○), FR3 (□), commercial Piscos A (▲), B (●), IND (■).

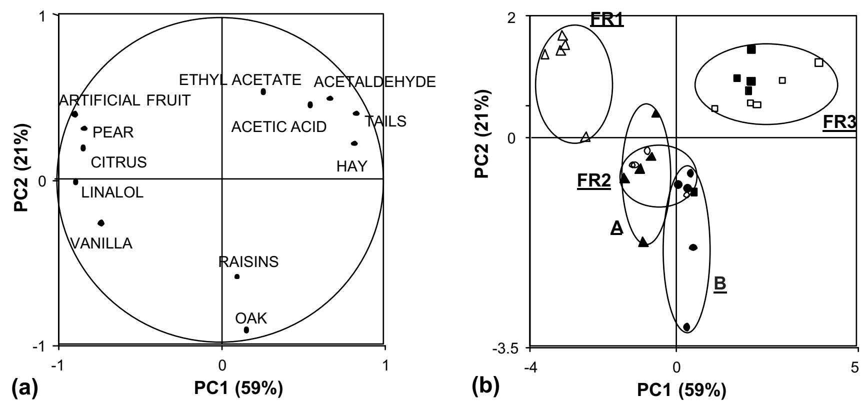

Fig. 2. First two principal components of PCA on aroma sensory scores. (a) Attribute loadings, (b) sample plot including distillate fractions FR1 (Δ), FR2 (○), FR3 (□), commercial Piscos A (▲), B (●),IND (■).

citrus and artificial fruit) from products with vegetal and chemical notes (hay, distillation tails and acetaldehyde). Consequently, the major differentiation of the products was made on fruity and terpenic properties, which are frequently considered as positive notes, in contrast to vegetal and chemical notes that are frequently considered as defects. In addition, the second principal component (PC2) differentiated products with oak and raisins olfactory notes (and also caramel and vanilla odours) from products with chemical notes, especially ethyl acetate.

Odour and aroma first factorial sample plots (Figs. 1b and 2b) were very similar. The three types of fractions, FR1, FR2 and FR3, were differentiated into three clusters. FR1 samples presented high intensities in artificial fruit, ethyl acetate, citrus and linalol; FR2 samples shared common characteristic notes for linalol, vanilla, citrus; and FR3 samples were judged intense on tails and, to a lesser extent, on hay and acetaldehyde attributes. SNK confirmed the previous differentiation among fractions. FR1 samples were grouped into the highest artificial fruit note cluster for odour and aroma mode. FR3 samples belonged to the cluster with the highest scores on tail attribute for both tasting modes. Commercial Piscos were not clustered into a separate group, but were located between FR2 and FR3 samples along PC1 and opposed to FR1 samples along PC2. Piscos coming from distilleries A and B, both with similar negative co-ordinates on PC2 (like FR2) were scattered in the lower section of the PCA sample map. However, Piscos A appeared to present stronger terpenic-fruity notes together with caramel and vanilla notes and Piscos B stronger oak and raisins notes. SNK confirmed the differentiation between A and B samples. For linalol odour, three A samples were grouped in the highest intensity cluster and three B samples in the lowest intensity cluster. For linalol aroma, A and B samples were separated into two significantly different clusters. In addition, the majority of B samples were classified within a group of high scores for oak odour and aroma, while part of A samples were classified in a cluster with low scores for both modes. The rest of the commercial Piscos (IND), coming from different distilleries, showed some clustering in the positive side of PC1 and PC2, close to FR3 samples (with chemical-vegetal notes). Nevertheless, some of these products appeared closer to B samples.

Three-factor ANOVA [2] showed no significant effect of the tasting mode, except for the linalol attribute. Overall, the tasting mode did not induce consistently higher or lower intensities over the majority of samples and subjects (Table 2). For linalol attribute, 19 samples (out of 29) were perceived as more intense when assessed orthonasally. Significant interactions between product and tasting mode on three attributes (tails, ethyl acetate and linalol) showed that some products were perceived differently by the panel according to the tasting mode.

Table 2
Tasting mode, product mode and subject mode F-ratios of the 3 factor ANOVA [2] performed on odour and aroma scores

Descriptor	Tasting mode	Product ×mode	Subject ×mode
Acetaldehyde	3.15	1.23	9.45***
Tails	0.14	1.78**	8.07***
Acetic acid	2.60	1.12	11.34***
Ethyl acetate	0.10	2.02*	10.98***
Oak	0.06	1.36	5.33***
Caramel	0.09	0.83	6.48***
Vanilla	0.14	1.29	7.38***
Raisins	0.23	0.93	5.94***
Citrus	2.52	1.31	2.56**
Pear	0.35	0.81	5.48***
Artificial fruit	0.09	1.39	3.95***
Linalol	5.29*	1.82**	1.78
Hay	0.24	1.06	4.95***
Degrees of freedom	1	28	11

*, **, *** indicate attribute significance at $P < 0.05$, $P < 0.01$, $P < 0.001$, respectively.

ANOVA [3] enables a deeper insight to be gained of the interactions between product and tasting mode. Two attributes showed significant product effects: linalol and ethyl acetate. For linalol attribute, one FR1 and one FR2 sample presented respectively the lowest and the highest intensity difference between odour and aroma (−1.2 and 1.4, respectively). One IND sample and one FR1 sample presented extreme values for odour minus aroma scores for ethyl acetate (−1.0 and 1.2, respectively).

3.2. Comparison of subject scoring of odour and aroma attributes

Although both tasting modes offered a similar number of attributes enabling the panel to significantly differentiate the products (significant product effect), F-ratios associated with the product effect were higher for odour attributes in a majority of cases (Fig. 3). Only five attributes (raisins, pear, vanilla, oak and linalol) presented higher F-ratios for aroma attributes.

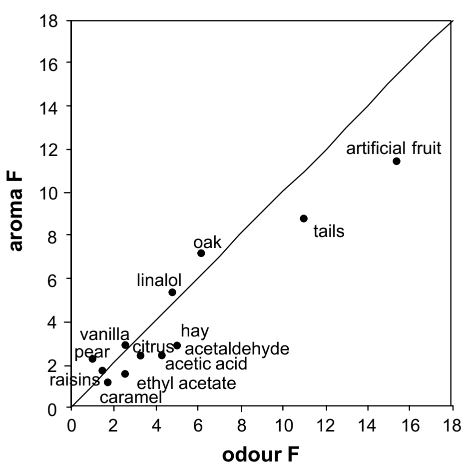

Fig. 3. Product F-ratios of aroma attributes versus F-ratios of odour attributes resulting from two-factor ANOVA [1].

ANOVA [4] gave a better insight into subject performances. The mean F-ratios per attribute (averaged over all subjects) showed that a majority of attributes had higher ratio values in odour than in aroma (Fig. 4a) corroborating former results at a panel level (Fig. 3). Attributes with the largest difference in favour of odour discrimination were citrus, linalol, raisins, pear and distillation tails. Oak and vanilla presented the highest value for aroma, though not very distant from the symmetry line. Contrasting the latter with the panel results, linalol, pear and raisins presented different behaviours, showing that panel and individual discrimination were quite similar for the majority of attributes, but not directly comparable in all cases. For example, at a panel level the samples were better differentiated regarding the linalol aroma. Individually, a greater number of subjects significantly discriminated the products according to the linalol odour, with eight and six discriminant subjects for the odour and aroma mode, respectively.

Mean F-ratios per subject (Fig. 4b) also showed a clear trend for higher discrimination on the odour mode. Only three subjects, s4, s5 and s10, presented higher F-ratios on aroma. Aroma F-ratios were comprised between 1 and 3, in contrast, odour F-ratios ranged from 1.5 to 4, with s1 having an F-ratio close to 6. The number of discriminant attributes ($P < 0.1$) per subject ranged between two and nine on aroma, and between four and nine on odour, with s1 showing the highest discrimination abilities (13 odour attributes).

Further analysis of subject performance by ANOVA [2] showed that almost all attributes presented significant interactions between subjects and tasting modes. This shows that the magnitude of the intensity difference between modes varied among subjects. This was confirmed by the subject effects in ANOVA [3] and associated SNK. Some subjects scored the products significantly higher in odour or aroma for a majority of attributes. It was especially the case of s1, s2, s3, s6, s7,

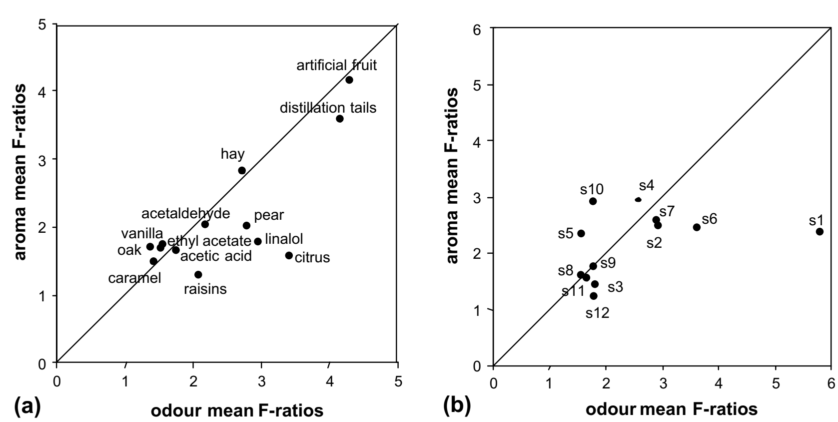

Fig. 4. Aroma versus odour F-ratios from one-factor ANOVA [4]. (a) Averaged over attributes and (b) averaged over subjects.

s12 on odour and s4, s5 and s10 on aroma. The only exception was linalol, for which almost all the subjects (11 out of 12) scored higher in the odour mode.

3.3. Prediction of aroma profile from odour profile

Correlation coefficients (r) between tasting modes per attribute ranged from 0.34 for ethyl acetate to 0.91 for artificial fruit (Fig. 5). Acetaldehyde, distillation tails, oak, artificial fruit, linalol and hay led to the highest correlation coefficients ($r > 0.7$). The remaining attributes ($r < 0.6$) presented greater scoring differences between the two tasting modes.

In order to obtain a better prediction of one tasting mode from another, and since odour assessment led to a better sample discrimination and also limited the subject sensory fatigue, a PLS predictive model of aroma from odour data was developed for each attribute. Good prediction of aroma scores with quite low PRESS values close to $VAR_{attribute}$ values were obtained except for oak attribute (Table 3). The number of PLS factors used for each predicted attribute was not superior to 3. $VAR_{attribute}$ ranged between 0.16 for hay and 0.29 for acetic acid. PRESS values ranged between 0.06 for pear and 0.75 for oak. The ratios $PRESS/VAR_{attribute}$ were lower than, or close to, 1 for the majority of attributes, showing that the prediction did not induce higher errors than those associated to the profiling methodology. Nevertheless, oak attribute presented a ratio value of 3.65, indicating that prediction was not acceptable.

The first four predictors (odour attributes) of greatest influence on each aroma attribute model are shown in Table 4. Considering all the predictive models, odour attributes with the highest weights were tails, linalol, artificial fruit, hay, citrus and ethyl acetate.

4. Discussion

4.1. Products

Twelve out of 13 attributes were significantly discriminated in both tasting modes indicating that the selected attributes, and the training aided by standards allowed good product differentiation performance.

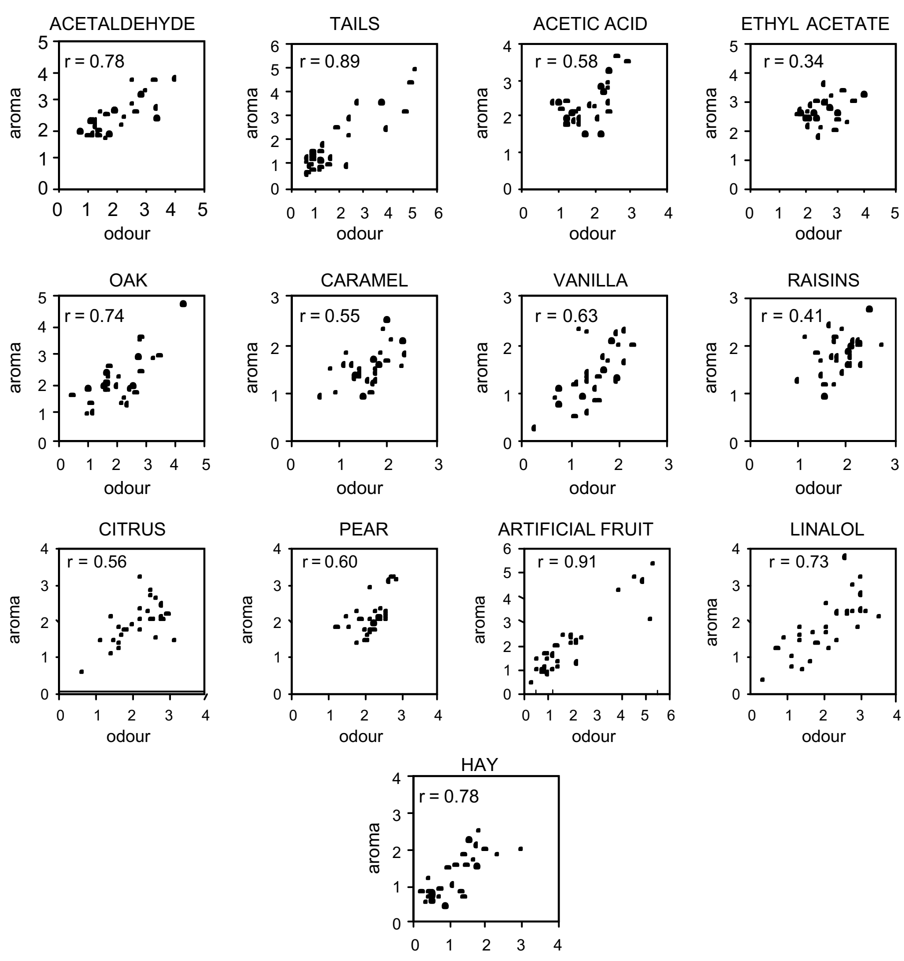

Fig. 5. Product aroma mean scores versus odour mean scores (r = correlation coefficient).

Table 3
PLS models for the prediction of each aroma attribute from the whole set of discriminant odour attributes

Aroma descriptor	PLS factors[a]	$VAR_{attribute}$[b]	PRESS[c]	PRESS/$VAR_{attribute}$ ratio	r[d]
Acetaldehyde	2	0.25	0.27	1.06	0.71
Tails	3	0.22	0.27	1.22	0.91
Acetic acid	3	0.29	0.31	1.07	0.64
Ethyl acetate	2	0.24	0.19	0.78	0.26
Oak	2	0.21	0.75	3.65	0.64
Vanilla	1	0.17	0.21	1.26	0.71
Raisins	2	0.16	0.08	0.51	0.53
Citrus	2	0.19	0.09	0.48	0.82
Pear	1	0.21	0.06	0.28	0.80
Artificial fruit	1	0.20	0.11	0.55	0.86
Linalol	2	0.19	0.12	0.63	0.84
Hay	2	0.16	0.24	1.54	0.78

Table includes measured data characteristics ($VAR_{attribute}$), model characteristics (PLS factors) and model performance (PRESS, PRESS/$VAR_{attribute}$ ratio, r).
[a] Number of factors of the model determined by minimising the PRESS value.
[b] Variance of the aroma mean.
[c] Mean of aroma squared prediction errors calculated on the test data set.
[d] Correlation between predicted and observed data.

Table 4
First four predictors (odour attributes in decreasing order: odour 1, 2, 3, 4) of highest influence in the PLS prediction model of each aroma attribute

Aroma attribute	Odour 1	Odour 2	Odour 3	Odour 4
Acetaldehyde	Tails (+)	Linalol (−)	Citrus (−)	Acetaldehyde (+)
Tails	Linalol (−)	Tails (+)	Acetaldehyde (−)	Ethyl acetate (−)
Acetic acid	Hay (+)	Oak (−)	Artificial fruit (−)	Tails (−)
Ethyl acetate	Ethylacetate (+)	Hay (+)	Oak (−)	Artificial fruit (+)
Vanilla	Tails (−)	Artificial fruit (+)	Linalol (+)	Citrus (+)
Raisins	Citrus (+)	Acetaldehyde (−)	Linalol (+)	Hay (+)
Citrus	Artificial fruit (+)	Ethyl acetate (+)	Tails (−)	Acetaldehyde (+)
Pear	Artificial fruit (+)	Tails (−)	Linalol (+)	Hay (−)
Artificial fruit	Artificial fruit (+)	Tails (−)	Linalol (+)	Hay (−)
Linalol	Artificial fruit (+)	Tails (−)	Ethyl acetate (+)	Oak (−)
Hay	Tails (+)	Linalol (−)	Vanilla (−)	Citrus (−)

Coefficient sign (+, −) indicates positive or negative contribution to the aroma attribute, respectively.

Correlations between sensory attributes within each mode were high. Sensory associations were very similar regardless of the tasting mode. They may result from the concomitant presence in the product of volatile compounds inducing different perceptions. For example, linalol and artificial fruit odours have been reported to show high correlation with concentrations of linalol and esters (ethyl octanoate, ethyl hexanoate and isoamyl acetate) respectively (Peña y Lillo et al., 2003). Moreover, these compounds were pointed out as possible odour impact molecules in Pisco spirits. FR1 samples contained high concentrations of both types of compounds and presented high intensities of linalol and artificial fruit notes. In addition, the high correlation between linalol and citrus notes could be explained by the sensory similarity of these terpenic notes. Indeed, linalol molecule is often a main constituent of essential oils giving citrussy sensory notes (Anupama, Asha, Ravi, Shanthi, & Rajalakshmi, 2001).

Samples were mainly differentiated according to the type of distillation fraction. As regards FR3 samples, fractions obtained the closest to the distillation tails during the process, were clustered near the distillation tail attribute. Conversely, FR1 fractions, containing highly volatile molecules such as linalol, ethyl octanoate, ethyl hexanoate and isoamyl acetate, were described by fruity notes generally associated to these compounds (Arctander, 1994). Commercial Piscos are usually blends of different distillation fractions. The results suggest that FR1 samples were used in low proportion in the blending, or/and that their sensory characteristics, like artificial fruit notes were masked by the olfactory notes of the other distillate fractions, according to possible odour suppression phenomena in mixture (Laing, 1994).

Piscos A and B appeared to result from distillation protocols similar to FR2 samples, and in contrast, most of IND Piscos were similar to FR3 samples. These results evidenced that the tail cut of some IND samples was probably done later in the distillation process compared to commercial Piscos A and B. Moreover, IND Piscos were quite largely scattered on PCA maps, indicating differences in their production process. In addition, commercial Piscos could also be differentiated along a maturation axis described by the oak note. This olfactory perception probably resulted from the contact between most commercial Piscos and either oak barrels or oak chips during the maturation process. Commercial Piscos with the strongest maturation process (A and B) were thus clustered close to oak attribute. It is worth noting that raisins had a high loading on PC2 and a high correlation with oak, suggesting a possible sensory association between oak and raisins.

The similarity observed in attribute use and product differentiation in odour and aroma modes corroborated the findings of other authors in water solutions containing one aroma compound (Burdach et al., 1984) and in red wines (Aubry et al., 1999a). No tasting mode led to significantly higher perceived intensities at a panel level for the complete set of samples except for linalol. This result contrasted with the findings on red Burgundy wines (Aubry et al., 1999a), where 11 out of 20 attributes present a tasting mode effect (six with higher odour mean scores and five with higher aroma mean scores). In the latter study, the two tasting modes were used within the same session. In contrast, in the present study, samples were assessed using only one tasting mode during a session, which limits possible bias due to sensory fatigue. However, for linalol attribute, the majority of samples were perceived as consistently less intense when assessed retronasally. Voirol and Daget (1986) showed that the vapour phase is delivered less efficiently by the retronasal route than by the orthonasal route because of the lower air flux that passes from the mouth to the nasal epithelium. Moreover, Linforth, Martin, Carey, Davidson, and Taylor (2002) found that when swallowing a liquid solution, the nose-space concentration is much smaller than static headspace concentration for 28 molecules tested in water. Mass transfer from the liquid to the gas phase is pointed out as the limiting factor. This reduction is compound specific since it depends on the mass transfer from the solution to the gas phase and absorption in the nasal epithelium. In particular, linalol concentration decreases by more than 90%. Besides, a reduction of olfactory perception intensity in mouth has been reported for sweetened model solutions, when olfaction and gustation are addressed simultaneously (Burdach et al., 1984). Kuo, Pangborn, and Noble (1993) have discussed the complexity of the phenomenon and its compound specific behaviour. Vanillin perceived intensity is enhanced by sucrose addition and depressed by citric acid and by NaCl, but citral intensity increases with the addition of tastants such as citric acid. Hence, gustatory and or/ trigeminal interactions with olfaction could also have caused the decrease in linalol aroma intensity observed in our study.

Some products were perceived differently by the panel according to the tasting mode (product-tasting mode interaction) on tails, ethyl acetate and linalol. Similar interactions between products and tasting modes were also found on red Burgundy wines (Aubry et al., 1999b). Chemical composition varied among products, not only regarding their potential olfactory stimuli but probably also gustatory and trigeminal stimuli. Consequently, the compound specific sensory interactions previously argued between olfactory perception and taste or trigeminal sensations may have affected only or more intensely the products for which the two types of perceptions were strongly perceived by the panel. Besides, saliva has a compound specific effect on volatile compounds and may cause either retention or release into the gas phase, modifying the headspace concentration (Van Ruth, Grossmann, Geary, & Delahunty, 2001). Nevertheless, Linforth et al. (2002) showed that dilution with saliva in mouth is not crucial to aroma delivery from the mouth to the nose-space. Yet, the solutions studied were immediately swallowed, which was not the case in our sensory tastings. Subjects kept the product in mouth a few seconds before spitting it, which possibly amplified the effect of saliva dilution.

4.2. Subjects

The lower discrimination ability of the panel for aroma compared to odour mode can be partially explained by the results of Pierce and Halpern (1996) who reported poorer discrimination abilities in vapour phase input by the retronasal route than by the orthonasal route. Sensory profiling of Burgundy wines (Aubry et al., 1999a; Sauvageot & Vivier, 1997) showed a higher panel discrimination in odour than in aroma mode, especially for "fruity" attributes. The present study highlighted that the largest discrimination ability in favour of the odour mode concerned artificial fruit attribute. Globally, individual performance showed coherent results with panel performance with a better sample differentiation by the odour mode. Aubry et al. (1999b) also reported similar individual discrimination abilities for both tasting modes, but a better odour discrimination at the panel level.

Subject-mode interactions showed that intensity scoring differences between modes varied among subjects. This observation may result from interindividual differences in sensitivity to flavour active compounds (Burdach et al., 1984; Kuo et al., 1993) or trigeminal active compounds (Cometto-Muniz & Hernandez, 1990; Green, 1996), tasting habits as mouth movements and spitting (Burdach & Doty, 1987), or consumption habits (Schifferstein & Verlegh, 1996). Our findings were in agreement with the preponderance of subjects over products in the differences between odour and aroma tasting modes found for red Burgundy wines (Aubry et al., 1999b) and confirmed the large interindividual variability in olfactory acuity observed in model solutions (Burdach et al., 1985).

4.3. Prediction

Several attributes showed low correlation coefficients between the two modes, evidencing clear differences between the two modes at a panel level. Even though high interindividual variability was observed, the panel behaviour was quite consistent regarding sample discrimination for both modes. Consequently, modelling the average behaviour of the panel using this data should lead to a robust model. The PLS model which uses linear combination of odour attributes to predict each aroma attribute revealed good performance for all attributes, except oak. No higher error was produced when predicting than when sampling. Overall, the validity of PLS models built on the distillation fraction data showed that relationships between odour and aroma within distillation fractions and between odour and aroma within more complex Pisco samples were similar. However, oak aroma was badly predicted, with a PRESS value 3-fold higher than $VAR_{attribute}$. The PLS model fitted with non-matured samples (14 samples, coming from three distillate fractions, FR1, FR2, FR3) was not able to predict the aroma of matured samples (15 commercial samples, coming from three distilleries, A, B and IND). To overcome the bad performance of the model relative to oak aroma, a new PLS model was built restricted to samples likely to present this olfactory note associated to a maturation step, i.e. A, B and IND Pisco samples. The PRESS value calculated by a leave-one-out cross-validation procedure decreased to 0.44, still leading to a $PRESS/VAR_{attribute}$ ratio higher than 2, and not permitting an adequate prediction. Consequently, no strong linear correlation between oak aroma and odour attributes seemed to exist. But, a non-linear relation between oak aroma and vanilla odour was demonstrated (Fig. 6), which corroborates the well-documented relation between oak and vanilla attributes in wines (Aiken & Noble, 1984; Francis, Sefton, & Williams, 1992).

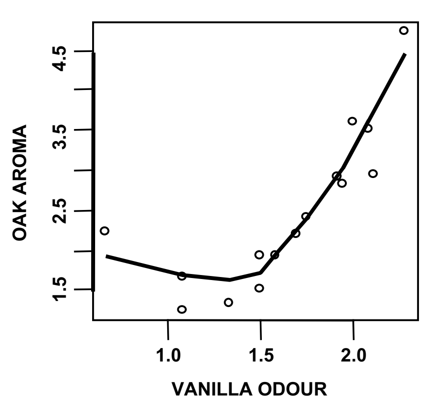

Fig. 6. The non-linear relationship between oak aroma and vanilla odour. Only A, B and IND Piscos are plotted. Line represents smooth values.

For a majority of attributes (tails, acetic acid, vanilla, raisins, citrus, pear and linalol), PLS models improved the correlation between predicted and observed aroma scores. Regarding ethyl acetate attribute, the correlation coefficients between the observed odour and aroma data and between PLS predicted aroma and observed aroma scores were lower than 0.34. This bad prediction could be due to the lower discriminant power ($P = 0.09$) of ethyl acetate aroma attribute. Concerning acetaldehyde, artificial fruit and hay attributes, the high correlations between odour and aroma panel scores were not enhanced by PLS models, but remained fairly constant. PLS models exhibited a good predictive power and are known to be more robust than the univariate linear model obtained by simple regression between odour and aroma of the same attribute. Indeed, PLS models use redundancy of different sensory attributes.

The predictors (odour attributes) of higher influence in each aroma model are in agreement with the correlations observed in the PCA performed independently on odour and aroma scores. The most influencing odour attributes corresponded to the positive (tails and hay) and to the negative (artificial fruit, linalol and citrus) extremes of PC1. Ethyl acetate, with positive coordinates on PC2 also presented quite high weights in PLS models. In addition, the low number of dimensions required by the predictive models ($\leqslant 3$) to optimally predict aroma agreed with the large data variance accounted for by the PCA first two dimensions.

5. Conclusions

Odour and aroma sensory profiles were obtained for Chilean Pisco samples. Selection of a relevant set of attributes used by well trained subjects, allowed to similarly differentiate the products, mainly according to their distillation fractions and degree of maturation. The panel was slightly more discriminating when assessing odour. Intensity score differences between modes were mainly due to subjects and, to a lesser extent, to products. These observations may be explained by differences in individual sensitivity, by compound specific variations in retronasal delivery and by sensory interactions between olfactory/gustatory/trigeminal perceptions.

Aroma profile was predicted from odour profile using PLS. Consequently, olfactory protocols can be optimised for Pisco spirits since their olfactory evaluation can be restricted to odour assessment, which is less tiring for subjects. For clustering purposes, no further data processing is required since odour and aroma are similar. Besides, although PLS has already been used to model data coming from human responses, applications have mainly served to explain and predict food preference from sensory characteristics (Huon de Kermadec, Durand, & Sabatier, 1997; Martens, Martens, & Wold, 1983). The present work is a promising new application of PLS to prediction of one set of sensory perceptions from another.

The direct applicability of these results to other spirits is limited by the use of Pisco specific terminology. Nevertheless, since they share common characteristics such as the hydro-alcoholic solution and maturation process, the fitting of an analogous model is promising.

Finally, future research for a better understanding of olfactory perception in spirits, such as Chilean Pisco, should address the following points: (1) the study of non-linearities determining specific perceptions, such as oak aroma, (2) the physicochemical behaviour of aroma components in the hydro-alcoholic solution and (3) the relation between product composition and product-associated perceptions. Such topics are currently investigated by our group.

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