Chem. Senses 30: 209–217, 2005

doi:10.1093/chemse/bji016

Perceptual Interactions in Odour Mixtures: Odour Quality in Binary Mixtures of Woody and Fruity Wine Odorants

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Abstract

The qualitative perceptual interactions in three binary mixtures of wine odorants were studied: isoamyl acetate (fruity note)/whisky lactone (woody note), ethyl butyrate (fruity note)/whisky lactone (woody note) and ethyl butyrate (fruity note)/guaiacol (woody note). For each binary mixture, the perceived quality and intensity of 24 stimuli (four supra-threshold concentration levels of each of the two compounds and their 16 possible combinations) were evaluated in five replications by a trained panel of 13 subjects. The application of the Olsson predictive model for odour intensity and quality perception gave quite a good estimation of the evolution of single component identification in the mixture when the intensity proportion of unmixed components varied. However, this model was unable to account for the odour quality dominance in mixtures of iso-intense components. An alternative linear logistic model was proposed to study the qualitative dominance of the woody note in the three mixtures when the perceived intensities of each unmixed compound were equal.

Key words: binary mixtures, linear logistic model, odour quality, Olsson's predictive model, wine odorants

Introduction

Grape variety, climatic conditions, viticultural practices, soil and region compose a complex system of aroma compounds that form the specific flavour character of each wine. The influence of some of these factors on wine aroma perception has been demonstrated by sensory descriptive analyses (Noble *et al.*, 1984; Heymann and Noble, 1987). However, gas chromatography–mass spectroscopy analyses of volatile compounds in wines have shown that odorants with major sensory impact resulting from fermentation and wood maturation are common to all grape varieties, but are present at different concentration levels and proportions depending on the wine. It could thus be hypothesized that these differences in concentration and proportion of the same odorants in mixtures generated various qualitative and quantitative sensory perceptions that may be responsible for the huge aromatic bouquet differences between wines. A previous study, which studied the relationship between 'appellation' and the typicity of Chardonnay wines, showed that when the woody note increased, flavour complexity of wine decreased (Moio *et al.*, 1993). Indeed, the intensity of fruity notes was especially reduced. In addition, it has been reported that ester compounds are responsible for the fruity aroma in wines and some lactones and volatile phenols contribute to the woody character (Ferreira *et al.*, 1998; Moio *et al.*, 1994; Chatonnet *et al.*, 1990).

The variety of sensory perceptions observed when mixing several odorants could be the result of qualitative (odour quality) and quantitative (odour intensity) perceptual interactions between odorants in mixture (Laing *et al.*, 1984). This suggests that in wine, perceptual interactions between fruity and woody notes may account for the previously observed sensory perceptions (Moio *et al.*, 1993). However, perceptual interactions between volatile compounds in combination remain difficult to predict in wines, and even in synthetic solutions. In order to overcome this difficulty, several mathematical models have been developed over the last thirty years to study and to predict the quantitative interactions in binary mixtures on the basis of perceived odour or taste intensities of the unmixed components at supra-threshold level (Berglund *et al.*, 1973; Patte and Laffort, 1979; Frijters, 1987; Laffort, 1989; Laffort and Dravnicks, 1982; Thomas-Danguin and Chastrette, 2002). Nevertheless, over the same period of time, only a few studies have dealt with both the perceived intensity and the quality of odour

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mixtures (Moskowitz and Barbe, 1977; Laing and Willcox, 1983; Laing *et al.*, 1984; Olsson, 1994), and only hypothetical rules have been proposed. According to these latter studies, if both odorants have approximately equal unmixed intensities, both are perceived in the mixture, whose quality seems to be intermediate between the qualities of its unmixed components (Moskowitz and Barbe, 1977; Laing and Willcox, 1983; Laing *et al.*, 1984; Olsson, 1994). These observations were confirmed by using a predictive model for odour intensity and quality perception (Olsson, 1994, 1998). This interaction model is the only model that predicts both the qualitative and the quantitative characteristics of a mixture on the basis of the intensities of its unmixed compounds. However, none of these studies included a systematic evaluation of perceptual interactions induced by odorants found mixed 'naturally' in food or beverages.

Therefore, in order to test the hypothesis that perceptual interactions could account for the sensory impact of woody notes on fruity ones in wine, the present study aimed to evaluate, in a model system, the perceptual interactions between woody odorants and fruity esters, both considered as key odorants in wine. Olsson's interaction model was used to predict the odour quality of the mixtures and the results were compared with experimental observations.

Materials and methods

Stimuli

Four odorants of wine were studied. The first two odorants have a major oak wood origin: β-methyl-γ-octalactone (generally called whisky lactone, W), described as woody and coconut, and methoxy-2-phenol (generally called guaiacol, G) described as woody and medicinal. The other two odorants were two esters: ethyl butyrate (B), described as fruity, strawberry or pineapple, and isoamyl acetate (A), described as fruity or banana. All odorants were obtained from Aldrich (France). The studied binary mixtures were composed of one woody and one fruity odorant: isoamyl acetate/whisky lactone, ethyl butyrate/whisky lactone and ethyl butyrate/guaiacol.

These odorants were chosen because (i) they are responsible for the woody or fruity notes in wine; and (ii) they exhibited 100% chemical purity with no odorous impurities detected when using gas chromatography–olfactometry (GC-O) with three trained subjects.

Four different concentration levels of each odorant were used (Table 1). For each odorant, the lowest concentration (C1) was first determined experimentally with the panel and corresponded to two times the highest individual perception threshold in order to ensure that all subjects could detect all concentrations. Individual perception thresholds of the four odorants had been previously evaluated by triangular tests. The next three concentrations in the liquid phase (C2, C3 and C4) were obtained by multiplication of the lowest concentration by a constant factor: 2.5 for whisky lactone, 9.0 for guaiacol, 6.7 for ethyl butyrate and 4.7 for isoamyl acetate. These factors were selected after preliminary trials undertaken on each odorant to choose four concentrations that were differentiated and approximately iso-intense.

Stimulus delivery hardware and Tenax trap analysis

Teflon® bags (49 × 49 cm, 20 l capacity, equipped with a Teflon® connector; Interchim France) were chosen to deliver the odorant. This static olfactometry technique and material were chosen because of their suitability in flavour analysis (Pet'ka *et al.*, 2000), and because they allowed for a large number of evaluations over several days without concentration modifications (Atanasova *et al.*, 2003). Solutions for sensory analyses were made in purified water (MilliQ system, Millipore®, France). Electrical resistance of the purified water was 18 MΩ/cm. The volume of solution in the bags was 250 ml. The bags were filled with pure nitrogen for 3 min and were prepared 12 h before the first measurement, to ensure equilibrium between the liquid and the gas phase. During the experiment, bags were stored, and the evaluations conducted in a quiet room with natural light and a temperature between 20 and 22°C.

In order to measure headspace concentrations of odorants in the bags, Tenax trapping was performed. The amount of each odorant present in the headspace sample was determined using calibration curves. Experimental desorption and analysis parameters have been described elsewhere (Atanasova *et al.*, 2003). Concentrations in the liquid phase and their corresponding concentrations in the gas phase are presented in Table 1.

Table 1 Concentrations of the odorant solutions in the liquid phase, their corresponding concentrations in the gas phase and mean of panel perceived odour intensity of unmixed odorants in the gas phase

Odorant	Concentration in the liquid phase (mg/l_{H_2O})				Concentration in the gas phase (μg/l_{N_2})				Mean of panel perceived odour intensity in the gas phase			
	C1	C2	C3	C4	C1	C2	C3	C4	I1	I2	I3	I4
Whisky lactone	4.0	10.0	25.0	63.0	0.1	0.26	0.54	1.52	1.46	3.27	5.39	7.9
Guaiacol	0.06	0.54	4.9	44.0	0.003	0.02	0.18	1.52	1.30	3.11	5.06	7.73
Ethyl butyrate	0.13	0.9	5.8	39.0	0.6	4.4	28.2	180.2	1.23	3.30	5.56	8.45
Isoamyl acetate	0.38	1.8	8.4	39.0	1.7	8.5	41.2	170	1.38	3.23	5.66	7.92

Subjects

Thirteen volunteers (nine women and four men, ranging in age from 20 to 42 years), with no allergies or self-reported problems in their sense of smell participated in the experiment. They were selected from 43 candidates based on the absence of anosmia to the odorants used in the present study, and according to their performance in classifying five different concentrations of 1-butanol in increasing odour intensity. All 13 subjects had previous experience in olfactory tests, as they had participated in sensory tests elaborated to evaluate the olfactory threshold of the four studied odorants and to choose the intensity measurement method (Atanasova *et al.*, 2004a). The subjects were not informed of the aim of the experiment. They were asked to avoid smoking, drinking and eating at least 1 h before each session.

Subjects were paid for their participation in the study (7.26 €/h). At the time of their recruitment, they were informed that they would have to smell different volatile compounds found in wine or in other food products. They were also informed of the experimental protocol before the beginning of the experiment.

Experimental procedure

Prior to the measurement session, a 1 h familiarization procedure was carried out on a separate day in order to familiarize the subjects with binary mixture odour intensity and quality rating. Both odorants (according to the studied mixture) were presented at their weakest and strongest concentration levels (C1 and C4) as well as in their four corresponding mixtures. Subjects had to evaluate both stimulus intensity and quality. The task and the instructions given to the subjects were identical to those given during the measurement sessions and are described below.

In the measurement sessions, each mixture type was studied during two sessions of ~1 h each taking place on separate days. There were 24 stimuli per mixture: four concentration levels of each odorant (fruity and woody) and their 16 possible combinations. Each stimulus was presented five times. Presentation order was balanced across repetitions and was identical for all subjects. The task for the subjects was twofold because perceived odour intensity and identification of perceived quality were studied simultaneously.

In terms of the quantitative aspect, subjects had to evaluate the overall perceived odour intensity of the binary mixtures and the perceived odour intensity of each unmixed odorant. Intensity ratings were made using a modified 1-butanol reference scale procedure (ASTM, 1975; AFNOR, 1996; Atanasova *et al.*, 2004a). The methodology used was a direct line scaling technique based on five memorized references of 1-butanol intensity levels. These 1-butanol references consisted of five concentration levels, selected in a preliminary experiment, in order to cover the intensity range of all odorants used. These concentration levels were carefully chosen in order to produce equal intervals in terms of perceived intensity (Atanasova *et al.*, 2004a). Before each measurement session, the subjects smelled the five intensity references of 1-butanol and were instructed to memorize them. To overcome the risk of adaptation and possible perceptual interaction between the studied odorant and 1-butanol, subjects were allowed to smell the bottles containing the 1-butanol reference odour before each measurement session only and not during the evaluation. During the experiment, subjects rated perceived intensity on a 13 cm line scale labelled at each end (zero intensity to very strong intensity) and structured by five equally spaced figures (1–5) corresponding to the five levels of 1-butanol intensity references. The resulting intensity was expressed in a score ranging from 0 to 13. Considering the direct scaling procedure used and the fact that the 1-butanol references elicited perceived intensities that were equidistant in terms of intensity perception, it could be considered that the scale respects both interval and ratio properties, at least in the range used by the subjects, i.e. not too close to the ends of the graphic scale. Moreover it was checked in a pre-study using the same methodology and the same panel that the score given to a blank stimulus on this scale was not statistically different from 0.

As far as the qualitative aspect is concerned, the subjects' task was to identify the perceived odour quality of each stimulus (unmixed odorant or mixture). For example, in an ethyl butyrate (B)/whisky lactone (W) mixture, subjects could choose one of the five responses: 'fruity', 'woody', 'fruity and woody', 'nothing' or 'another odour'.

Data acquisition was carried out using FIZZ software (Biosystèmes, Couternon, France).

In the present paper, only the qualitative responses will be studied. The study of intensities has been presented elsewhere (Atanasova *et al.*, 2004b).

Olsson's interaction model

Olsson's model (1994) specifically predicts identification probabilities such as:

$$p_{\mathrm{fruity}} = I^2_{\mathrm{fruity}} / (I^2_{\mathrm{fruity}} + I^2_{\mathrm{woody}})$$

and

$$p_{\mathrm{woody}} = I^2_{\mathrm{woody}} / (I^2_{\mathrm{fruity}} + I^2_{\mathrm{woody}})$$

where I_{fruity} and I_{woody} are the perceived intensities of the unmixed fruity and woody odorants respectively. According to this model, the probability of identifying a mixture as either fruity or woody is related to the perceived intensities of the components presented separately. Specifically, p_{fruity} equals p_{woody} when the component odours are iso-intense out of mixture. In 1998, the Olsson model was further developed and generalized (Olsson, 1998). We did not apply this new model to the present data however because it assumes the same symmetry as the 1994 model.

Linear logistic model

A linear logistic model was used to model the probability of fruity (respectively woody) responses according to the fruity intensity proportion in the mixture, τ. τ is the ratio between the perceived intensity of one of the odorants (fruity in our case) and the sum of the perceived intensities of each unmixed odorant:

$$\tau = I_{\text{fruity}}/(I_{\text{fruity}}+I_{\text{woody}})$$

It reflects the relative intensity proportion of one odorant, compared with the sum of the intensities of both odorants. When $\tau = 0.5$, the mixture is composed of iso-intense unmixed components.

This linear logistic model was fitted using individual numbers of fruity (respectively woody) responses, assumed to be distributed according to binomial distributions. It supposes that the relationship between the logit of fruity (respectively woody) response probability and τ is linear, and that the intercepts vary according to subjects [number of fruity responses ~ binomial distribution ($n = 5$; p_{fruity}); number of woody responses ~ binomial distribution ($n = 5$; p_{woody})]:

$$\text{logit}(p_{\text{fruity}}) = \log\left(\frac{p_{\text{fruity}}}{1-p_{\text{fruity}}}\right) = \mu + \alpha_{\text{subject}} + \beta(\tau - 0.5), \quad (1)$$

with the constraint:

$$\sum_{\text{subjects}} \alpha_{\text{subject}} = 0$$

$$\text{logit}(p_{\text{woody}}) = \log\left(\frac{p_{\text{woody}}}{1-p_{\text{woody}}}\right) = \mu' + \alpha'_{\text{subject}} + \beta'(\tau - 0.5), \quad (2)$$

with the constraint:

$$\sum_{\text{subjects}} \alpha'_{\text{subject}} = 0$$

μ (μ' respectively) is the mean panel intercept i.e. the value of logit(p_{fruity})(logit(p_{woody})respectively) at $\tau = 0.5$. The intercept for each subject is $\mu + \alpha_{\text{subject}}$ ($\mu' + \alpha'_{\text{subject}}$ respectively) and β (β' respectively) is the panel slope.

In order to study 'fruity and woody' responses, a logistic model (logit $p_{\text{fruity and woody}}$) (logit ($p_{\text{woody}}$) respectively) of three parameters was used: intercept, slope and curvature. The intercept, slope and curvature were not assumed to vary from one subject to another.

$$\text{logit}(p_{\text{fruit and woody}}) = \log\left(\frac{p_{\text{fruity and woody}}}{1-p_{\text{fruity and woody}}}\right) = \mu'' + \beta''(\tau - 0.5) + \gamma''(\tau - 0.5)^2 \quad (3)$$

where μ'' is the panel intercept, β'' is the panel slope and γ'' is the panel curvature.

Graphical data representations

Qualitative responses estimated with Olsson's and linear logistic models were reported on a graph developed by Olsson (1994), so as to compare the results visually. In this graphical representation, the probability of giving a 'woody' response is plotted against τ, as well as the probability of giving a 'fruity' response (Figures 1 and 2). In the graphical representation of the linear logistic model, the 'fruity', 'woody' or 'fruity and woody' responses are plotted versus τ. For 'fruity' and 'woody' responses, the effects are sigmoidal, because their probabilities lie between 0 and 1. For 'fruity' and 'woody' responses, the model reflects a linear effect in logit scale, with an intercept depending on the subject and a common slope. If we had represented the logit of response probabilities versus τ, we would have observed parallel straight lines with intercepts varying according to subjects. In Figure 2, only the panel probabilities are represented (parameters μ, β, μ', β'), giving a unique sigmoidal curve. As far as 'fruity and woody' responses are concerned, the effect is quadratic on the logit scale, giving an effect such as those shown in Figure 2 on the probability scale.

Data analysis

All statistical analyses were conducted using SAS® (SAS Institute Inc., Cary, NC), release 8.1. Linear regression analysis were performed using the GLM procedure. The linear logistic model was fitted with the GENMOD procedure.

In order to study the dominance of the odorant, the overlapping of the intercepts' ('fruity' and 'woody' responses) confidence intervals at $\tau = 0.5$ was used. This calculation of the confidence intervals (CI) gives an indication of the statistical significance ($\alpha = 0.05$) of the dominance.

Each CI was estimated through an independant modelling of experimental data subsets : one for the 'fruity' probabilities, one for the 'woody' probabilities and one for the 'fruity and woody' probabilities. Thus, despite the correlation between the data used to calculate p_{fruity}, p_{woody}, $p_{\text{fruity and woody}}$ and their CIs, the comparison between the probabilities using the CIs is allowed.

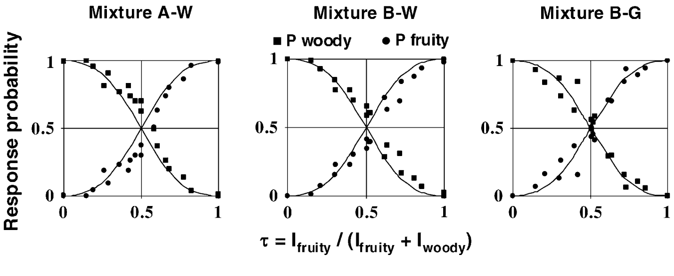

Figure 1 Qualitative 'woody' and 'fruity' response probabilities versus τ. The mean 'woody' (respectively 'fruity') experimental probability corresponded to the 'woody' (respectively 'fruity') experimental and response probabilities plus half of the mean over subjects of the 'fruity and woody' experimental and response probabilities (symbols). Fitted curves represent the response probabilities calculated response probability with Olsson's model.

Results

The aim of the experiment was to study, from a qualitative point of view, the perceptual interactions between woody and fruity olfactory notes.

First of all, considering stimulus quality evaluation, the term 'another odour' (one of the five proposed answers 'fruity', 'woody', 'fruity and woody', 'nothing', 'another odour') was never chosen. The answer 'nothing' was chosen only two times, that is to say a frequency of use of <0.6%. These two answers were consequently disregarded and only the 'fruity', 'woody' and 'fruity and woody' answers were analysed.

To study odour quality interactions, the individual experimental probability (p_{fruity}, p_{woody} and $p_{\text{fruity and woody}}$) of 'fruity', 'woody' and 'fruity and woody' responses were represented versus the relative odorous compound intensity, τ (Figures 1 and 2, symbols).

As expected, the probability of identifying the quality of the mixture as fruity (respectively woody) increased as the fruity (respectively woody) odorant intensity added to the mixture increased.

Empirical model for odour intensity and quality perception

The empirical model for odour intensity and quality perception (Olsson, 1994) was applied to obtain the mean of the individual probability of 'fruity' and 'woody' responses ($\mathrm{p}_{\text{fruity}}$ and $\mathrm{p}_{\text{woody}}$) calculated from the unmixed intensities of the two components. Inasmuch as the model was not designed to account for the 'fruity and woody' responses, Olsson (1994) recommended adding $\mathrm{p}_{\text{fruity and woody}}$ proportionally to $\mathrm{p}_{\text{fruity}}$ and $\mathrm{p}_{\text{woody}}$. The modelling results are reported graphically in Figure 1 (curves).

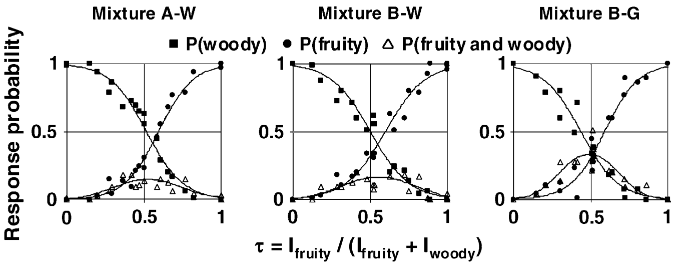

Figure 2 Qualitative 'woody', 'fruity' and 'fruity and woody' experimental response probabilities versus τ. The mean values of the subjects of 'woody' (respectively 'fruity' and 'fruity and woody') experimental response probabilities are represented with different symbols. Fitted curves represent the response probabilities obtained with linear logistic model.

Linear regressions were performed between calculated and experimental probabilities of 'fruity' and 'woody' responses for the three binary mixtures. Determination coefficients (R^2) obtained were very high ($R^2 \geq 0.98$), (Table 2).

According to Olsson's model, for mixtures of iso-intense components, the fruity response probability is equal to the woody response probability ($\mathrm{p}_{\text{fruity}} = \mathrm{p}_{\text{woody}}$ for $\tau = 0.5$) i.e. the curves of $\mathrm{p}_{\text{fruity}}$ and $\mathrm{p}_{\text{woody}}$ are symmetrical compared with the vertical line at $\tau = 0.5$. However, the graphical examination of experimental data (Figure 1, symbols) suggests that for mixtures of iso-intense components, the probability of identifying the mixture as fruity is smaller than the probability of identifying the mixture as woody ($\mathrm{p}_{\text{fruity}} < \mathrm{p}_{\text{woody}}$ for $\tau = 0.5$). In other words, the relationship between $\mathrm{p}_{\text{fruity}}$ and τ, and between $\mathrm{p}_{\text{woody}}$ and τ are not symmetrical compared with the vertical line at $\tau = 0.5$. This trend is clear at least graphically (Figure 1, symbols) for the binary mixtures of isoamyl acetate/whisky lactone and ethyl butyrate/whisky lactone.

An alternative model: a linear logistic model

In order to evaluate the statistical significance of the previously observed trends, an alternative linear logistic model was applied on odour quality experimental data. The linear logistic model can be applied to each of the three types of responses 'fruity' (equation 1), 'woody' (equation 2) and 'fruity and woody' (equation 3). Thus, the experimental probability $\mathrm{p}_{\text{fruity}}$, $\mathrm{p}_{\text{woody}}$ and $\mathrm{p}_{\text{fruity and woody}}$ were modelled separately (Figure 2, symbols). The modelling results are presented graphically in Figure 2 (curves). The determination coefficients (R^2) between experimental and calculated 'fruity' and 'woody' response probabilities exceeded 0.97 for the three mixtures. The R^2 calculated for 'fruity and woody' responses were also high ($R^2 \geq 0.64$, Table 2).

Using the linear logistic model, the hypothesis of no dominant odorant was statistically tested. This hypothesis implies the equality of 'woody' and 'fruity' probabilities of response for mixtures of iso-intense components ($\tau = 0.5$). Consequently, according to this hypothesis, for each mixture type the model intercept ('woody' or 'fruity' probabilities of response at $\tau = 0.5$) may not depend on the subject, and may

Table 2 Determination coefficients (R^2) between calculated and experimental probabilities of 'fruity', 'woody' and 'fruity and woody' responses

Response	Mixture A-W		Mixture B-W		Mixture B-G	
	Olsson's model	Linear logistic model	Olsson's model	Linear logistic model	Olsson's model	Linear logistic model
Fruity	0.98	0.99	0.98	0.98	0.99	0.97
Woody	0.98	0.99	0.98	0.98	0.99	0.98
Fruity and woody	–	0.73	–	0.64	–	0.86

be equal for both odorous compounds. Note that we first considered that there could be a difference in individual slopes and intercepts in the linear logistic model. However, there was an overlap of the 95% CIs of the individual slopes. Finally, then, we did not take individual slopes into account in the model. On the contrary, there was no overlap of the 95% CIs of individual intercepts; thus an intercept value depending on the subject was retained in the model.

Results of linear logistic modelling of responses for the three types of mixtures confirmed that p_{fruity} and p_{woody} at $\tau = 0.5$ depend on the subject ($P < 0.001$). Furthermore, the results for the three binary mixtures showed that the 95% CIs of the panel intercept (μ and μ') of the two odorants did not overlap (Table 3). More precisely, for the three mixtures, when unmixed odorants were present at iso-intense levels ($\tau = 0.5$), the mean probability of identifying the mixture as fruity was smaller than the mean probability of identifying the mixture as woody ($p_{\mathrm{fruity}} < p_{\mathrm{woody}}$ at $\tau = 0.5$). Obviously, this finding implied that the curves were not symmetrical with respect to $\tau = 0.5$ (Figure 2). However, Figure 2 showed that this observation seemed to be less marked for the ethyl butyrate/guaiacol mixture. For the ethyl butyrate/guaiacol mixture, the mean probability of answering 'fruity' was 0.28 at $\tau = 0.5$, whereas the mean probability of answering 'woody' was 0.33 at the same τ value. The difference was significant, but moderate compared with those observed for the other two mixtures.

When modelling the 'fruity and woody' responses, all the linear logistic models (equation 3) showed a negative and significant curvature ($P < 0.001$), but a non-significant slope ($P > 0.05$). The highest probability of identifying both the fruity and woody components in the mixture was two times higher in the case of the ethyl butyrate/guaiacol mixture ($p_{\mathrm{fruity\ and\ woody}} = 0.33$), as in the case of the acetate/whisky lactone mixture ($p_{\mathrm{fruity\ and\ woody}} = 0.15$) and the butyrate/whisky lactone mixture ($p_{\mathrm{fruity\ and\ woody}} = 0.16$). For the isoamyl acetate/whisky lactone and ethyl butyrate/whisky lactone mixtures, the 'fruity and woody' responses were the most frequent when τ values were slightly higher than 0.5 ($\tau = 0.55$ for the isoamyl acetate/whisky lactone mixture, $\tau = 0.56$ for the ethyl butyrate/whisky lactone mixture; Figure 2). Concerning the ethyl butyrate/guaiacol mixture, the maximal 'fruity and woody' response rate was observed at $\tau = 0.52$. This finding confirms that for this type of mixture, the dominance of woody notes is less marked than for the two other types of mixtures.

In order to study the sharpness of the shift between the identification of the mixture as fruity or woody only, the probabilities of answers 'fruity', 'woody' and 'fruity and woody' were compared at the τ-value where the proportions of 'fruity' and 'woody' responses were equal. This τ-value at 'exact intermediacy' (Olsson, 1993) corresponded to the intersection point (IP) of the two curves fruity alone and woody alone (Figure 2). The overlapping of 95% CIs on probabilities of 'fruity' = 'woody' and 'fruity and woody' responses was especially tested for the three types of mixtures at this τ-value corresponding to IP. The calculation and the comparison of the confidence intervals give an indication concerning the perception of the mixture as 'fruity' and 'woody' or 'fruity and woody' simultaneously.

For both the isoamyl acetate/whisky lactone mixture and the ethyl butyrate/whisky lactone mixture, at this IP point, there is no overlap of the 95% CIs on the mean probabilities of 'fruity' or 'woody' responses and 'fruity and woody' responses (Table 4). However, for the ethyl butyrate/guaiacol mixture there is an overlap of the 'fruity' or 'woody' responses and 'fruity and woody' responses (Table 4). These results show that in the case of the ethyl butyrate/guaiacol mixture only, subjects are able, for some mixture proportions, to more frequently identify the two odours simultaneously. In the case of the isoamyl acetate/whisky lactone and ethyl butyrate/whisky lactone mixtures, most of the subjects were able to identify only one of the two odours, whatever the mixture proportion and even for mixtures of iso-intense components.

Discussion

The results obtained in this study confirmed that the perceived quality of a binary mixture, in terms of identification probability, is clearly dependent on the τ-ratio of the perceived intensities of the unmixed components (Olsson, 1994; Schifferstein and Kleykers, 1996; Olsson, 1998). Following up on this idea, previous studies have shown that the relative intensities of the unmixed components were of primary importance in determining which qualities were to be perceived in the binary mixture (Laing and Willcox, 1983). Thus, when both single odorants were of

Table 3 Intercept of 'fruity' and 'woody' response with 95% CIs ($\mathrm{CI_{min}}$ = lower boundary of the CI and $\mathrm{CI_{max}}$ = upper boundary of the CI) for the three studied mixtures

Response probability	Mixture A-W			Mixture B-W			Mixture B-G		
	Intercept	$\mathrm{CI_{min}}$	$\mathrm{CI_{max}}$	Intercept	$\mathrm{CI_{min}}$	$\mathrm{CI_{max}}$	Intercept	$\mathrm{CI_{min}}$	$\mathrm{CI_{max}}$
Fruity	0.27	0.23	0.31	0.26	0.23	0.30	0.28	0.24	0.32
Woody	0.54	0.50	0.58	0.52	0.47	0.56	0.36	0.33	0.40

Table 4 Intersection point (IP) of 'fruity' and 'woody' curves generated by the linear logistic model with 95% CIs (CI_{min} = lower boundary of the CI and CI_{max} = upper boundary of the CI) for the three studied mixtures

Response probability	Mixture A-W			Mixture B-W			Mixture B-G		
	IP	CI_{min}	CI_{max}	IP	CI_{min}	CI_{max}	IP	CI_{min}	CI_{max}
Fruity = woody	0.40	0.35	0.44	0.38	0.34	0.42	0.32	0.28	0.36
Fruity and woody	0.15	0.12	0.18	0.16	0.09	0.19	0.33	0.29	0.37

approximately equal intensity, both odorants appeared to be recognized in the mixture (Laing and Willcox, 1983; Laing *et al.*, 1984; Moskowitz and Barbe, 1977). Furthermore, it has been argued that in that case of mixtures of iso-intense components, the perceived quality was exactly intermediate between the qualities of the unmixed components (Olsson, 1993). This idea is inherent in Olsson's predictive model, where the probability of identification of both components was predicted to be the same for mixtures of strict iso-intense components (Olsson, 1994, 1998).

However, it was demonstrated in several cases that, in a mixture, intensity proportions (τ) of the unmixed components were not always good predictors of the perceived quality of the mixture (Senouci, 2003). Indeed, in binary taste or odour mixtures, one component could dominate (Laing and Willcox, 1983; Schifferstein and Kleykers, 1996). Moskowitz (1976) noted that binary mixtures of equal unmixed intensity components smell 'either entirely like one of the components' or 'are intermediate between the two'. However, a re-examination of these results suggested that unmixed components in Moskowitz's study were not iso-intense (Laing and Willcox, 1983).

Our findings shed some light this discrepancy in that we showed that perceptual interactions could lead to a dominance of the perceived quality of one component which was not related to a higher intensity proportion of this unmixed component ($\tau > 0.5$). Indeed, the results presented above indicated that for the three fruity–woody mixtures studied, there was a dominance of the woody qualitative component in binary mixtures of iso-intense components. This dominance, demonstrated through a linear logistic modelling of experimental data, was in particular shown at $\tau = 0.5$, i.e. for mixtures of 'true' iso-intense components. It has to be underlined that the kind of analysis we used is heavily dependent on the ratio properties of the quantitative scaling methodology. In the present study, we used a new scaling method and we checked in a preliminary experiment (Atanasova *et al.*, 2004a; unpublished data) that this method accounts for both interval and ratio properties at least in the range used by the subjects. Moreover, ratio properties of the scale were confirmed *a posteriori* by the correct position of the mixtures, including iso-intense components at τ values of ~ 0.5.

Application of the Olsson predictive model for odour intensity and quality perception gave quite good estimations of single component identification in the mixture when the intensity proportions of unmixed components varied. However, by its construction, this model was not able to account for the dominance in odour quality in mixtures of iso-intense components. In addition, the Olsson predictive model did not take into account the identification proportion of both components at the same time in the mixture (Olsson, 1994). Our methodology of data analysis, on the other hand, allowed us to conduct a separate analysis of this type of dual quality identification. Interestingly, the results indicated that for isoamyl acetate/whisky lactone and ethyl butyrate/whisky lactone mixtures, most subjects were unable to identify both components, even when equal intensity levels of the two components were mixed. Consequently, a sharp change in quality identification from 'woody' to 'fruity' was thus demonstrated when the proportion of fruity compound increased in the mixture. These observations were in agreement with those of Laing and Willcox (1983). However, in the case of the ethyl butyrate/guaiacol mixture, it appeared to be easier for most of the subjects to identify both components when equivalent intensity levels of the two components were mixed. It seems relevant to note that this last mixture also exhibited the lowest dominance of the woody note.

Earlier cases of dominance of a quality in mixtures of iso-intense components have been observed. In the field of gustation, Schifferstein and Kleykers (1996) reported a qualitative dominance of sucrose over citric acid. In the field of olfaction, Olsson (1993) re-analysed Lawless's (1977) results on mixtures of lavender oil and pyridine. He showed that equal intensities of mixed components did not correspond to equal intensities of unmixed components. This implies a qualitative dominance of the lavender odour over the pyridine one. Olsson suggested explanations for this finding, citing the pleasantness and unpleasantness of the components. Laing (1983) also studied mixtures of odorants with opposite hedonic characters (*trans*-2-hexenal and *trans*-2-decenal) and found that the quality of mixtures of iso-intense components was not exactly intermediate between the qualities of the components but seemed to be closer to the *trans*-2-hexenal quality. This strongly suggested a dominance of the *trans*-2-hexenal quality. Results from a recent study showed that unpleasant odorants are judged more quickly than pleasant odorants (Bensafi *et al.*, 2002). This difference in temporal treatment could obviously be a basis of the dominance of a quality in mixtures of iso-intense components, but in that case, the unpleasant odour should dominate. However, in our study, both woody and fruity components were usually perceived as pleasant (Arctander, 1969a,b). Therefore, the qualitative dominance could not be supported only by the hedonic character opposition of the components of the mixture.

Several psychophysical studies on odour or taste mixtures have suggested that perceptual interactions could be observed when Steven's exponents of the components are different (Moskowitz, 1972; Bartoshuk, 1975; Bartoshuk and Cleveland, 1977; Laffort, 1994). These authors especially showed that the lower the Steven's exponent, the more that component is suppressed in mixtures. The Steven's exponents of the studied odorants were evaluated in preliminary experiments: whisky lactone, 0.38; guaiacol, 0.22; isoamyl acetate, 0.20; and ethyl butyrate, 0.19. It is thus interesting to note that the most marked dominance was observed in mixtures including whisky lactone, i.e. in mixtures where the two components differed the most in terms of Steven's exponent values.

Many studies have focused on whether perceptual interactions observed in mixtures are peripheral or central. Most of them concluded that interactions such as mixture suppression (in our case, dominance referred to an asymmetry in suppression) were mostly peripheral events (Bell *et al.*, 1987; Jinks and Laing, 1999; Duchamp-Viret *et al.*, 2003). Several hypotheses concerning mechanisms by which odorants might interact at the receptor level have been proposed. Some of these suggested that the odorants may be differentially adsorbed by the mucus according to their polarity (Laing, 1988). Thus, odorants of similar polarity would therefore be more suppressive of each other (Bell *et al.*, 1987). An odorant polarity could affect its rate of diffusion through the mucus to the receptor cells, such that 'slower' odorants would be more likely to be suppressed than 'faster' odorants (Laing and Mac Leod, 1992). As a result, mixtures of odorants with closer polarity values should interact in a more reciprocal way than odorants with different polarity values. These hypotheses seemed to be confirmed by our results. Indeed, higher woody dominance was observed in isoamyl acetate/whisky lactone and ethyl butyrate/whisky lactone mixtures where the differences between the estimated $\log P$ values of the components were higher than with ethyl butyrate/guaiacol mixture. The $\log P$ value (defined as the logarithm of the partition coefficient of solute between *n*-octanol and water) of odorants is 2.13 for isoamyl acetate, 1.70 for ethyl butyrate, 1.20 for guaiacol and 3.51 for whisky lactone. The lower the $\log P$ value of an odorant, the more polar that odorant is. The $\log P$ constant was estimated by the chemical software Windows Molecular Modelling Pro (version 2, ChemSW, Copyright James A. Quinn, 1992–2000). $\mathrm{Log}P$ estimations were made by molecular fragmentation in atoms. Consequently, it can be hypothesized that the qualitative dominance phenomenon could begin in the early events of olfactory coding at the receptor level. However, supplementary experiments are needed to validate this assumption.

The perceptual olfactory interactions between fruity and woody aroma compounds in wine were studied in laboratory conditions using psychophysical methods. Experimental data highlighted the qualitative dominance of the woody note in the three binary mixtures studied, when the perceived intensities of each unmixed compound were equal. From the point of view of wine perception, this dominance is in accordance with the observation of Moio *et al.* (1993) of a masking effect of a wine's esters by odorants brought by oak wood. Indeed, perceptual interactions, which take place due to complex mediums where several volatile and nonvolatile compounds are candidates for perception, could impact dramatically on the final product flavour. In the case of wine, taking into account these perceptual interactions could thus help wine producers, who focus on chemical composition, to increase the quality of the aromatic bouquet through, for example, a better control of aromatic notes of wine breeding in oak wood.

Acknowledgements

This work was supported by the INRA and the Burgundy Regional Council. We greatly acknowledge Mary Bouley and Daniel Martinez for reading this article.

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Accepted December 30, 2004