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Intensity and Persistence Profiles of Flavor Compounds in Synthetic Solutions. Simple Model for Explaining the Intensity and Persistence of Their Aftersmell

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Hydroalcoholic solutions containing a single aroma-active compound were evaluated by a sensory panel to determine the difference between ortho and retronasal odor intensities (ΔI_{ro}), buccal savoring, and aftersmell duration. Eight compounds were used. Buccal perception seems to be just a physiologically restricted form of retronasal perception. ΔI_{ro} values were dependent on the panel, although results from the two panels were significantly correlated. Such differences and the aftersmell persistence were also significantly correlated with different physicochemical parameters related to volatility. A simple model to explain such dependence is proposed. The model considers the mouth−throat system as a perfect mixing tank with a finite amount of odorants being progressively diluted by swallowing and purging (both taken as continuous processes). Retronasal intensity is modeled from the odor properties of the liquid in such a tank calculated from orthonasal odor intensity versus concentration (*I*/log *C*) curves. The model explains successfully experimental results and has also been successfully applied to instrumental data from other authors.

KEYWORDS: Odor; aroma; wine; orthonasal; retronasal; aftertaste

INTRODUCTION

A complete understanding of the chemical base of the aroma-related sensory characteristics of a product should, ideally, allow the researcher to predict the complete sensory properties of a solution containing a given odorant at a given concentration, including not only its orthonasal odor intensity but also its buccal and retronasal intensities and the duration of its aftersmell. This task would require, obviously, comprehension of, first, the physicochemical properties of the odorant with most influence on the way it is perceived and, second, the mechanism of delivery.

Two different paths can be taken to achieve such comprehension. One consists of the use of sensory analysis and the other one of the use of some instrumental device or strategy to measure how the odorants are released from the foodstuff to reach the olfactory epithelium. To date, the instrumental alternative has produced more reliable results than sensory analysis. In fact, the scarce sensory studies conducted on this issue are not conclusive and are even often contradictory. Voirol and Daget (*1*) found that retronasal threshold values were inferior to orthonasal thresholds for vanillin and citral. However, at suprathreshold concentrations they reported that the intensity was superior for orthonasal perception in the case of citral, whereas in the case of vanillin, the curve retronasal *I*/log *C* was superior to orthonasal for certain concentrations. The results of Kuo et al. (*2*) on the same compounds are consistent with those of Voirol and Daget, showing in general higher intensities for orthonasal perception than for retronasal (although in the case of vanillin the intensities were very similar). Similarly, Burdach et al. (*3*) and Miettinen et al. (*4*) observed that orthonasal intensities were higher, and Aubry et al. (*5*) reported higher intensity in orthonasal profiles in a wine profiling study for the majority of wine descriptors. On the contrary, Vuilleumier et al. (*6*) found retronasal intensities of linalool stronger than orthonasal ones, and Bertuccioli et al. (*7*, *8*) have demonstrated that retronasal properties and persistence are more discriminative than orthonasal properties for the evaluation of red wine quality.

A major part of the lack of agreement must be attributed to the difficulty linked to the measurement of retronasal odor intensities, affected by many factors that complicate the agreement between panels and experiments. A way to eliminate their influence is by using a single sensory panel, a fixed liquid matrix, a fixed set of instructions, and a set of odorants. Following this approach, Espinosa (*9*) has recently been able to show that there is a linear relationship between the volatility of the odorant (measured through log K_{aw}) and its retronasal/orthonasal (R/O) ratio in pure water. This ratio is the number of times the concentration must be increased to get retronasally the same intensity observed orthonasally. The higher the

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volatility, the higher the R/O ratio. To the best of our knowledge, there are no similar studies measuring persistence.

On the other hand, several instrumental studies have shown that volatility plays a major role in determining the persistence and relative retronasal intensities of a given odorant. Linforth and Taylor (*10*) used the atmospheric pressure chemical ionization (APCI) probe to measure the persistence of volatile compounds in the breath and demonstrated that persistence could be well predicted via an empiric model in which log *P* and vapor pressure of the molecule were the major terms (*11*). In a subsequent work, they found that the proportion of an odorant, relative to its headspace concentration (hs), in the mouthspace (ms) or in the nosespace (ns), was strongly correlated to the log of its K_{aw} partition coefficient (*12*). The ratios ms/hs or ns/hs should be, a priori, related to the ability of the compound to be perceived via the orthonasal or retronasal route. They further developed a semiempirical model for predicting such ms/hs or ns/hs measures. A similar dependence has been also noted by Van Ruth et al. (*13*) by using a mouth simulator. The role of volatility also appears, albeit indirectly, in the elegant work recently presented by Buettner (*14*). By using the BOSS technique, she found that the most persistent compounds in wine aroma perception are, in general, the most polar and least volatile.

Therefore, there are sound instrumental data demonstrating that the volatility of a compound, measured through log K_{aw} or log K_H (Henry's constant), plays an outstanding role in the persistence and relative ortho/retronasal properties of the odorants. However, there are not many data supporting that such a relationship holds for sensory measurements, particularly in the case of persistence. Another point that still needs further consideration is the nature of such a relationship. In particular, it is striking that the relationship between persistence, ns/hs, and R/O was linear, with log K_{aw} or log K_H, and not with K_{aw} or K_H themselves, which are the terms related to the concentration of the odorants in the vapor phases. In our opinion, this is a key question the answer to which can give important clues in the understanding and modeling of the odor properties of solutions containing an odorant.

The main objectives of the work presented here are, first, to confirm by sensory analysis if the relative ortho/retronasal properties of odorants in hydroalcoholic solutions are also related to volatility; second, to verify if such a relationship holds also for sensory measurements of persistence; and, third, to develop a simple model able to explain why persistence and relative ortho/retronasal intensities are linearly related to the logarithms of constants related to volatility (Henry's constant or gas liquid partition coefficient).

EXPERIMENTAL PROCEDURES

Chemicals. Nine aroma-active compounds of the highest purity available were chosen as examples of chemical groups relevant to flavor research. The olfactive purity of these chemicals was controlled by GC−olfactometry (GC-O). All of them were natural odorants and were tested at concentrations at which they can be found in wine and other natural products. Decanal, eucalyptol, linalool, methionol, and methyl vanillate were supplied by Aldrich (Gillingham, U.K.), ethyl 2-methylbutyrate and eugenol were from Fluka (Buchs, Switzerland), and δ-octalactone was from Lancaster (Strasbourg, France). β-Damascenone was a gift from Firmenich (Geneva, Switzerland). Water was obtained from a Milli-Q purification system (Millipore, Bedford, MA), and ethanol and tartaric acid were from Panreac (Montcada, Spain).

Sensory Analyses. In all cases the analyses were performed in a tasting room equipped with individual standard test booths. The sensory panel consisted of eight trained individuals (five women and three men), all of them were laboratory staff highly experienced in intensity ratings. All of the tests were carried out with tulip glasses containing 25 mL of the test sample closed with a lid. Each sample was made of synthetic wine (water; ethanol, 10% v/v; tartaric acid, 2 g L^{-1}; and pH adjusted to 3.4) and a given amount of analyte. For each of the analytes, four different samples were tested: three concentration levels (1 and 5× and 25×) plus a blank. The concentrations of the compounds in the samples were chosen so that the most intense of the three odor intensity scores (retronasal, buccal, or retronasal) of the most concentrated sample (25×) was between 60 and 90% of the full scale. Only one analyte was examined per session. The sensory analysis comprised two parts.

Familiarization. Panelists were first asked to sort five samples of synthetic wine by the intensity of the perceived odor. In all sessions, there was one blank sample (synthetic wine only), three test samples, and one sample containing the corresponding analyte at 3−4 orders of magnitude above the threshold concentration taken from ref *15* or calculated in the laboratory. This most concentrated sample served as an anchor reference for the highest intensity in the following part of the test. Samples were presented in a random order. Once the sorting task finished, the panelists were instructed to describe the perceived odor and memorize it.

Intensity Scaling. In the second phase the judges were asked to rate the intensity of the odor memorized in the sorting task. A modified 7-point labeled magnitude scale (*16*) (graphic scale with logarithmic elements described as follows: 0 = no odor, 1 = weak odor, of low intensity, 2 = clear perception of odor, intermediate intensity, 3 = extremely intense odor; the intermediary values did not bear any description) was proposed for use throughout the study. Only the three test samples and a blank sample were presented in a session, following a Latin square design. The concentrations of the solutions tested are seen in **Table 1**.

First, the judges rated the odor intensity of the memorized odor by nose (*orthonasal perception*). This test was made successively for all cups, with time gaps to prevent adaptation. Then they were asked to sip from the liquid, keep it in the mouth by swirling, savor it, and rate the odor intensity (*buccal perception*). After swallowing, the judges had to start the stopwatch and stop it when the perception of odor in mouth disappeared (*aftersmell persistence*). Additionally, they had to rate the maximum perceived intensity of the odor during this time (*retronasal perception*). They were not explicitly instructed to avoid further swallowing during this period, but to behave as in normal wine tasting sessions.

Purging Constant. A 150 mL volume of a synthetic wine containing the eight volatiles studied was poured into a bubbler flask. A stream of nitrogen was bubbled for 200 min through the solution at 100 mL min^{-1}. The volatile-enriched stream of nitrogen was passed through a trap consisting of a cartridge containing 400 mg of LiChrolut EN resin (Merck, Darmstadt, Germany). After this, volatiles were eluted with 3.2 mL of dichloromethane; 30 μL of internal standard (2-octanol, C = 700 ppm) was added to the extract, which was analyzed on a Fisons 8000 series gas chromatograph equipped with a flame ionization detector. The column used was a DB-Wax (J&W Scientific, Folsom, CA; 60 m × 0.32 mm × 0.5 μm). Chromatographic conditions were as follows: hydrogen as carrier gas (3 mL min^{-1}); splitless injection (splitless time 90 s); injection volume, 3 μL; injector temperature, 250 °C; detector temperature, 250 °C; temperature program 40 °C for 2 min, raised at 6 °C/min to 200 °C and held at this temperature for 15 min, then raised to 220 °C and held at this temperature for 20 min. Quantification was made on the basis of calibration graphs obtained for each compound. The efficiency of the trapping system was previously checked in different experiments aiming to ensure: 1st, that the breakthrough volumes of the different volatile compounds are not reached and, 2nd, that the elution of the retained compounds is complete.

The purging constant, K_p, was calculated as follows:

$$K_p = \frac{\log\left[\frac{W_0^i}{(W_0^i - W_e^i)}\right]}{t} \quad (1)$$

Table 1. Sensory Properties of the Analyzed Solutions: Mean Orthonasal, Buccal, and Retronasal Intensities (I) and Aftersmell Duration (T_P, Units in S), Together with the Corresponding Standard Error of the Mean (E)

compound	c (mg L^{-1})	I_{ortho}	E_{ortho}	I_{bucc}	E_{bucc}	I_{retro}	E_{retro}	T_P	E_{Tp}
eucalyptol blank	0	0.19	0.13	0.25	0.13	0.38	0.18	11.00	4.91
eucalyptol C1	1	0.50	0.19	0.53	0.24	0.44	0.15	17.80	5.04
eucalyptol C2	5	1.22	0.25	0.97	0.32	1.06	0.31	24.38	5.14
eucalyptol C3	25	2.06	0.11	1.81	0.35	1.69	0.31	47.50	7.21
mean		**1.26**	**0.18**	**1.10**	**0.31**	**1.06**	**0.26**	**29.89**	**5.80**
decanal blank	0	0.13	0.08	0.00	0.00	0.00	0.00	2.88	1.88
decanal C1	0.2	1.31	0.21	0.84	0.18	1.03	0.18	25.00	4.42
decanal C2	1	1.81	0.25	1.34	0.31	1.41	0.18	34.50	4.10
decanal C3	5	2.16	0.19	1.75	0.33	1.84	0.24	49.63	3.87
mean		**1.76**	**0.22**	**1.31**	**0.27**	**1.43**	**0.20**	**36.38**	**4.13**
ethyl 2-methylbutyrate blank	0	0.19	0.13	0.00	0.00	0.00	0.00	4.38	2.31
ethyl 2-methylbutyrate C1	0.2	0.69	0.26	0.38	0.21	0.38	0.21	12.75	5.09
ethyl 2-methylbutyrate C2	1	1.25	0.16	0.91	0.27	0.75	0.16	23.32	4.05
ethyl 2-methylbutyrate C3	5	2.13	0.21	1.44	0.32	1.50	0.25	39.50	6.54
mean		**1.35**	**0.21**	**0.91**	**0.26**	**0.88**	**0.20**	**25.19**	**5.23**
eugenol blank	0	0.38	0.21	0.50	0.27	0.38	0.21	9.50	5.27
eugenol C1	0.2	0.53	0.14	0.34	0.12	0.41	0.12	16.88	4.47
eugenol C2	1	1.00	0.41	0.88	0.41	1.06	0.37	24.00	7.76
eugenol C3	5	1.81	0.27	1.81	0.21	1.69	0.19	51.50	8.19
mean		**1.11**	**0.27**	**1.01**	**0.25**	**1.05**	**0.22**	**30.79**	**6.81**
linalool blank	0	0.44	0.20	0.25	0.16	0.28	0.15	11.38	5.21
linalool C1	0.4	0.84	0.16	0.63	0.23	0.72	0.20	18.63	5.26
linalool C2	2	1.13	0.32	1.00	0.30	1.06	0.29	27.63	4.46
linalool C3	10	1.81	0.30	1.63	0.32	1.63	0.25	43.88	9.84
mean		**1.26**	**0.26**	**1.08**	**0.28**	**1.14**	**0.24**	**30.04**	**6.52**
methionol blank	0	0.25	0.13	0.19	0.13	0.25	0.19	8.25	4.29
methionol C1	3	0.34	0.18	0.13	0.13	0.38	0.16	12.05	4.96
methionol C2	15	1.38	0.23	1.06	0.27	1.38	0.16	39.88	5.95
methionol C3	75	2.38	0.08	2.19	0.23	2.56	0.15	75.38	9.35
mean		**1.36**	**0.16**	**1.13**	**0.21**	**1.44**	**0.15**	**42.43**	**6.76**
methyl vanillate blank	0	0.64	0.17	0.64	0.26	0.64	0.28	16.38	5.27
methyl vanillate C1	8	0.29	0.14	0.50	0.18	0.64	0.24	21.36	5.18
methyl vanillate C2	40	0.39	0.10	1.00	0.29	0.93	0.21	30.21	6.98
methyl vanillate C3	200	1.43	0.12	1.79	0.27	2.21	0.17	83.86	15.68
mean		**0.70**	**0.12**	**1.10**	**0.24**	**1.26**	**0.21**	**45.14**	**9.28**
δ-octalactone blank	0	0.13	0.08	0.13	0.13	0.19	0.13	6.25	3.44
δ-octalactone C1	4	0.41	0.15	0.38	0.21	0.53	0.19	25.25	7.24
δ-octalactone C2	20	1.06	0.15	1.03	0.23	1.41	0.25	41.75	7.34
δ-octalactone C3	100	1.94	0.18	1.66	0.29	1.91	0.22	78.38	12.45
mean		**1.14**	**0.16**	**1.02**	**0.24**	**1.28**	**0.22**	**48.46**	**9.01**
grand mean		**1.24**	**0.20**	**1.08**	**0.26**	**1.19**	**0.21**	**36.04**	**6.69**

where W_0^i is the initial mass of compound i in the extractor, W_e^i is its mass in the extract, and t is the duration of the stripping process.

Data Treatment. A three-way ANOVA (balanced general linear model; factors judge, concentration, and perception) was used to compare intensities. Tukey's test served for pairwise comparisons within the factor judge and Bonferroni's test for the comparisons within factors concentration and perception (*17*). When aftersmell duration results were compared, a two-way ANOVA (factors judge and concentration) was carried out.

Estimation of Physicochemical Properties. Boiling point (bp), vapor pressure (ρ), Henry's law constant (K_H), water solubility (W_{sol}), and octanol−water partition (log P) were estimated by using the EPI Suite (*18*) (25 °C reference temperature).

Additionally, gas−liquid partition coefficients (GLPCs) were estimated from an empirical equation (*19*)

$$GLPC_{est} = \frac{10^5 RI_{ap}^{1.2}}{\Delta RI^{4.2}} \quad (2)$$

where RI_{ap} is the retention index of the compound on an apolar column and ΔRI a difference of retention indices measured on polar and apolar columns. Precise retention indices were taken from the SKAF flavor database from Farkas et al. (*20*).

RESULTS

Differences between Orthonasal and Retronasal Intensities in Hydroalcoholic Solutions. A primary objective of the present work was to study the differences between the relative intensities of the orthonasal, buccal, and retronasal pathways for a series of odorants dissolved in hydroalcoholic solutions. The complete set of sensory results is shown in **Table 1**, and the basic ANOVA statistics carried out on the set of data are shown in **Table 2**. A first observation that can be made is that buccal intensities are nearly always close to retronasal intensities, which suggests that buccal perception of odor is just a physiologically restricted form of retronasal perception. Because of this and the, in general, higher imprecision obtained in the measurement of buccal odor intensities, we will focus on the differences between orthonasal and retronasal pathways.

The last column in **Table 2** gives the average difference between the odor intensity scores obtained between the retronasal and orthonasal routes of olfaction for each of the compounds (ΔI_{ro}). A negative value for this parameter indicates that, on average, such a compound is perceived more intensely by the orthonasal route, whereas a positive value indicates the

Table 2. Three-Way ANOVA of Panel Intensity Measurements and Mean Difference between Retronasal and Orthonasal Perceptions[a]

	concn		judge		perception route		mean
compound	*F*	*p*	*F*	*p*	*F*	*p*	ΔI_{ro}
eucalyptol	33.9	<0.001	5.2	0.004	2.0	0.178	–0.198
decanal	25.2	<0.001	8.6	<0.001	12.2	0.004	–0.333
ethyl 2-methyl-butyrate	89.5	<0.001	17.9	<0.001	36.7	<0.001	–0.479
eugenol	67.7	<0.001	18.1	<0.001	0.5	0.499	–0.063
linalool	20.0	<0.001	11.3	<0.001	1.0	0.328	–0.125
methionol	244	<0.001	7.1	<0.001	0.9	0.366	0.073
methyl vanillate	54.6	<0.001	1.6	0.228	23.8	<0.001	0.560
δ-octalactone	104	<0.001	14.1	<0.001	3.2	0.097	0.146

[a] Results from two independent sensory experiments are given.

opposite. Differences, in general, were not very high, and, in fact, in only three cases (decanal, ethyl 2-methylbutyrate, and methyl vanillate) were they statistically significant (at $P < 0.05$). In any case, these mean differences (ΔI_{ro}) are significantly correlated with the volatility of the compounds or with other physicochemical parameters related to volatility, as can be clearly seen in **Table 3**.

All of these results confirm the major role of volatility in the relative sensitivity of the orthonasal and retronasal odor routes. Orthonasal olfaction is more sensitive to volatile and not very water-soluble compounds (ethyl 2-methylbutyrate), whereas retronasal olfaction is relatively more sensitive to the less volatile and/or very soluble compounds (methyl vanillate or methionol). These results are coincident with those presented by Linforth et al. (*12*) and with those recently presented by Espinosa (*9*).

Persistence of the Aftersmell. Average aftersmell persistence (T_P, arithmetic mean of panelists' data) and the corresponding standard errors of the mean are shown in **Table 1** and are also plotted on **Figure 1**. **Table 4** shows the results of a two-way ANOVA carried out on aftersmell duration data. Aftersmell duration was also examined to detect possible correlations with the different physicochemical properties presented in **Table 3**, and the results of the study are also shown in that table. As can be seen, in this case the best correlations are found between the aftersmell duration of the most concentrated solutions and the log of the purging constant, K_p, as is shown in **Figure 2** ($T_P = -8.3345 \times \log K_P + 25299$; $R^2 = 0.91$, $F = 67.4$, $P < 0.001$). This parameter is a different estimate of the volatility of the odorant, and its importance and significance are discussed later. This result is also coincident with those reported by Linforth and Taylor (*11*) and documents the existence of a strong

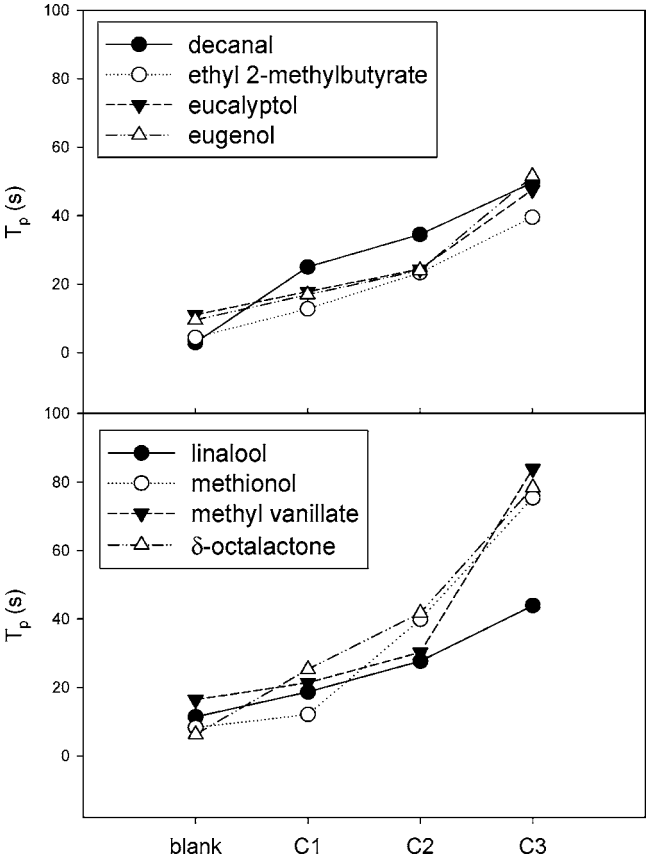

Figure 1. Aftersmell duration functions for eight compounds. C1, C2, and C3 refer to the concentrations of the solutions given in **Table 1**.

inverse relationship between the persistence of an odorant in the aftersmell and its volatility.

Therefore, the sensory results here presented confirm the previous reports about the role of volatility, measured by log K_H or log K_p, on the release of odorants contained in liquid solutions. However, it should be noted that, although it is not surprising that volatility was involved in retronasal perception, there is no sound basis to explain why such a relationship is with the logarithm of K and not with K itself, which is the parameter related to the concentration of odorant in the vapor phases. In the next part of the paper, we present a model able to explain the role of volatility in the relative ortho/retronasal properties and aftersmell duration of a given odorant.

Model for Aftersmell and Retronasal Odor Intensity. The premises under which the model lies are as follows.

Table 3. Physicochemical Properties of the Volatile Compounds Studied and Their Corresponding Coefficient of Determination (R^2) of Regression with the Mean Differences between Retronasal and Orthonasal Intensities (ΔI_{ro}) and Mean Duration of Aftersmell (T_P)

compound	bp (°C)	MW	W_{sol} (mg L^{-1})	log *p*	ρ (mmHg)	log K_H	log $GLPC_{est}$	RI_{DB-Wax}	log K_p
eucalyptol	174.1	154.2	332	3.13	1.56	–3.02	–1.003	1210	–2.78
decanal	216.1	156.3	43.5	3.76	0.24	–2.95	–1.831	1503	–1.96
ethyl 2-methylbutyrate	134.9	130.2	1070	2.26	8.03	–2.89	–1.345	1055	–1.66
eugenol	264.3	164.2	754	2.73	0.01	–5.57	–3.557	2174	–4.91
linalool	204.1	154.2	684	3.38	0.08	–4.61	–2.608	1560	–2.91
methionol	177.5	106.2	47450	0.44	0.28	–6.08	–3.582	1727	–6.33
methyl vanillate	285.7	182.2	1495	1.82	0	–6.99	–4.042	2613	–6.68
δ-octalactone	250	142.2	3632	1.59	0.03	–5.85	–2.388	1976	–5.81
determination coefficients with ΔI_{ro}									
R^2	0.56	0.13	0.04	0.27	0.35	0.83***	0.60*	0.79**	0.84***
determination coefficients with T_P									
R^2 (av)[a]	0.34	0.00	0.51	0.35	0.34	0.53	0.28	0.45	0.73**
R^2 (C_{max})[b]	0.34	0.00	0.49	0.54	0.25	0.72**	0.44	0.56	0.91***

[a] Average of persistence (as log T_P) for the three different concentrations studied. [b] Persistence of the maximum concentration studied.

Table 4. Two-Way ANOVA of Aftersmell Duration Measurements

	concn		judge	
compound	*F*	*p*	*F*	*p*
eucalyptol	9.0	0.003	1.9	0.154
decanal	14.6	<0.001	2.9	0.044
ethyl 2-methylbutyrate	9.3	0.003	2.4	0.081
eugenol	9.5	0.002	2.2	0.099
linalool	4.2	0.038	1.7	0.196
methionol	31.2	<0.001	2.6	0.063
methyl vanillate	10.4	0.002	1.3	0.316
δ-octalactone	14.3	<0.001	3.1	0.036

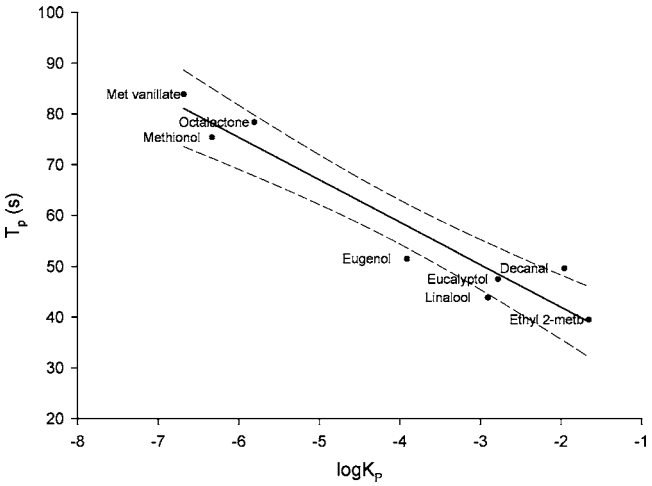

Figure 2. Average aftersmell durations (T_P) at the highest concentration levels as a function of logarithm of purge constant K_p.

First, after swallowing, there are two different places in which odorants still can be found: in the throat, forming a thin film, and in the mouth, forming a thicker film. The mouth is a major reservoir for volatiles.

Second, the transfer of volatiles to the olfactory epithelium takes place mainly by vaporization of the odorants placed in the throat, which in a relatively short time becomes depleted. However, such a film is renewed by a new small volume of saliva containing volatiles swallowed from the mouth. The concentration of the pool of odorants in the mouth decreases due to progressive dilution with saliva and further swallowing.

Third, for the sake of simplicity, the mouth−throat system will be considered as a single system, similar to a perfect mixing tank filled with a small and constant volume of liquid. There is a flow of liquid (saliva) getting into the tank with no concentration of volatiles, and a second flow of liquid flowing out (swallowing) with the concentration of volatiles present at that moment in the mouth−throat. Similarly, there is a constant supplement of gas free from volatiles and an equivalent output of gas carrying out volatiles released from the liquid present at that moment in the mouth−throat.

Fourth, the model will focus on the concentration of volatiles present in the liquid phase of this ideal mouth−throat system. Retronasal intensity and odor persistence will be modeled by assuming that both are related to the evolution with time of volatiles in the liquid phase of the ideal mouth and to the odor properties of such solutions.

Fifth, the last premise is that the odor properties of the liquid film can be interpreted by using the *I*/log *C* relationships obtained by orthonasal olfaction of solutions containing the odorants (**Table 1**).

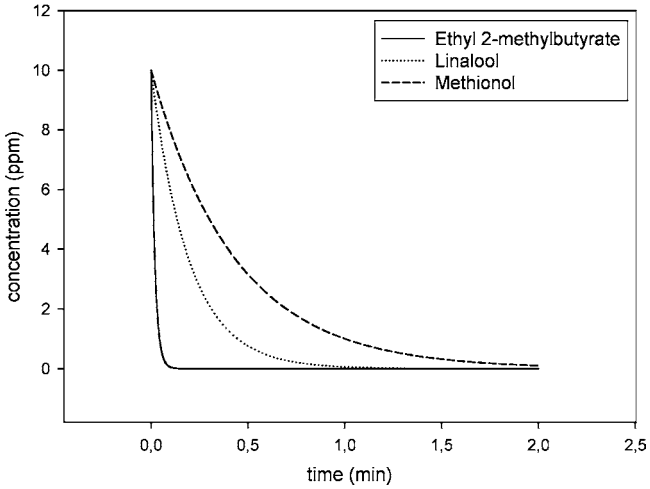

Figure 3. Predicted evolution of concentration of three volatile compounds with different volatilities in the mouth according to eq 1 and data in **Table 3**.

According to these ideas, the amount of volatile lost by swallowing (considered to be a continuous process) in time *t* is

$$-\frac{dC_i}{dt} = C_i\frac{\dot{F}}{V} \tag{3}$$

where C_i is the concentration of volatile in the mouth at time *t*, $\dot{F}$ is the flow of saliva and the average flow swallowed, and *V* is the volume of liquid in the mouth. Similarly, the amount of volatile lost from the liquid in the mouth by transference to the gas phase is

$$-\frac{dC_i}{dt} = K^i_{pm}C_i \tag{4}$$

where K^i_{pm} is the mouth purging constant for volatile *i*, which is related to the volatile Henry's constant, to the flow of air, to temperature, to some geometric features, and, eventually, to the mass transfer coefficient. C_i is the concentration of volatile in the mouth at time *t*.

The combination of both expressions makes it possible to state that the change of concentration of a given volatile at a given time in the liquid contained in the mouth is

$$-\frac{dC_i}{dt} = \left(K^i_{pm} + \frac{\dot{F}}{V}\right)C_i \tag{5}$$

The integration of this expression gives

$$\log C_{it} = \log C_{i0} - \frac{1}{2.303}\left(K^i_{pm} + \frac{\dot{F}}{V}\right)t, \tag{6}$$

where C_{it} is the concentration of volatile *i* at time *t* and C_{i0} is the concentration of that volatile at time 0.

Approximated parameters for this function have been estimated as follows: $\dot{F}$ has been taken as 1 mL min^{-1}, which is a normal saliva flow. *V* has been taken as 1 mL, which can be also considered as an "average" volume of liquid contained in the mouth after swallowing. K^i_{pm} values have been obtained from a dynamic headspace sampling system (K_P, see Experimental Procedures and **Table 3**) and have been used directly after normalization to the volume of gas pumped from the lung to the nostrils in average ($15 \times 100 = 1500$ mL min^{-1}) and to the volume of liquid (1 mL). Under these conditions $K_{pm} = 1000K_p$.

Table 5. Orthonasal Thresholds and Initial Concentrations Used for Modeling Persistence

compound	orthonasal threshold (ppm) (C_{ith})	C_0 (mg L^{-1})
decanal	0.0017	5
ethyl 2-methylbutyrate	0.074	5
eucalyptol	0.55	25
eugenol	0.158	5
linalool	0.132	10
methionol	2.5	75
methyl vanillate	0.195	200
δ-octalactone	0.71	100

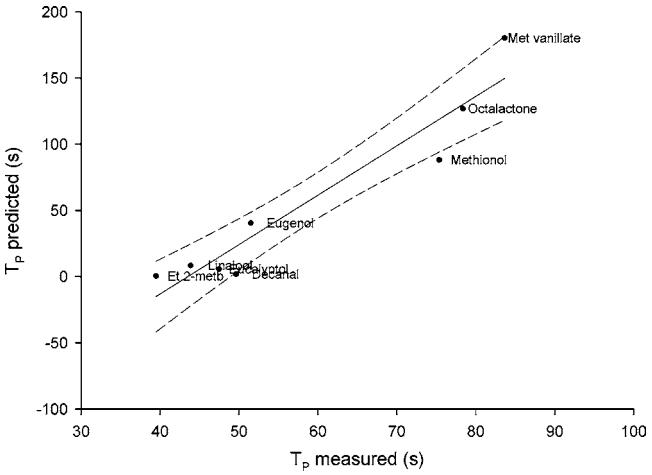

Figure 4. Aftersmell persistence predicted with eq 3 as a function of measured persistence.

Figure 3 shows the decrease of the concentration of three volatile compounds with different volatilities in the mouth according to eq 6 and data in **Table 3**. In all cases the initial concentration of these compounds was 10 ppm. As can be seen in the figure, the model predicts a residence time (time needed to virtually disappear) in the mouth after swallowing below 0.2 min for ethyl 2-methylbutyrate; this residence time is 1.1 min for linalool, whereas in the case of methionol >2 min will be needed for its actual concentration to become $^1/_{100}$ of its initial concentration.

Calculation of Persistence. To model persistence, we will use a practical definition of this parameter: The persistence of an odorant is the time at which the concentration of such odorant in the mouth equals the orthonasal odor threshold (C_{ith}). Thresholds have been directly calculated from the *I*/log *C* plots built with data in **Table 1** as the concentration at which the orthonasal intensity becomes the intensity of the blank and are shown in **Table 5**.

Therefore, persistence can be directly estimated from eq 6, making $C_{it} = C_{ith}$ and $t = T_P$.

$$T_P\,(\mathrm{s}) = \frac{2.303(\log C_{i0} - \log C_{ith})}{K^i_{pm} + \frac{\dot{F}}{V}}60 \qquad (7)$$

The values calculated with this equation are proportional to the experimental values (pred $T_P = 3.061T_P - 106$, with $R^2 = 0.820$, significant at $P < 0.002$), as shown in **Figure 4**.

Calculation of Retronasal Intensity. Retronasal intensity is going to be estimated by using a plot similar to the one presented in **Figure 3**, but in which orthonasal intensity, in addition to concentration, will be also plotted on the *Y* axis. Orthonasal intensity is calculated from the corresponding *I*/log *C* relationships. **Figure 5** illustrates how calculations were actually done. Evolution of the concentration of linalool or methionol with time was obtained from the following equation (exponential form of eq 6):

$$C_t = C_0 \times 10^{-(K_{pm}i+1)t} \qquad (8)$$

Next, the orthonasal odor intensities that such concentrations would produce at that time have been estimated by using the corresponding *I*/log *C* plots. These intensities are marked as odor intensity in the figures. The last curve (identified in the graphs as AOI × 10) represents the integral of the previous odor intensity versus time curve. In the case of linalool, for instance, the figure shows that a 10 ppm solution has a residence time of ~1.1 min, that the orthonasal intensities of the liquid film remaining in the mouth range from 1.7 (initial) to 0.03 (final), and that the accumulated odor intensity (AOI) is ~10. In the case of methionol, the residence time would be >2 min; however, as the odor threshold is reached at ~1 min, the area of the curve intensity versus time would be just ~7, less than that of linalool. Of course, the values given before were not intended to be exact, but rather to show differences between compounds. Our hypothesis is that the square root of such area,

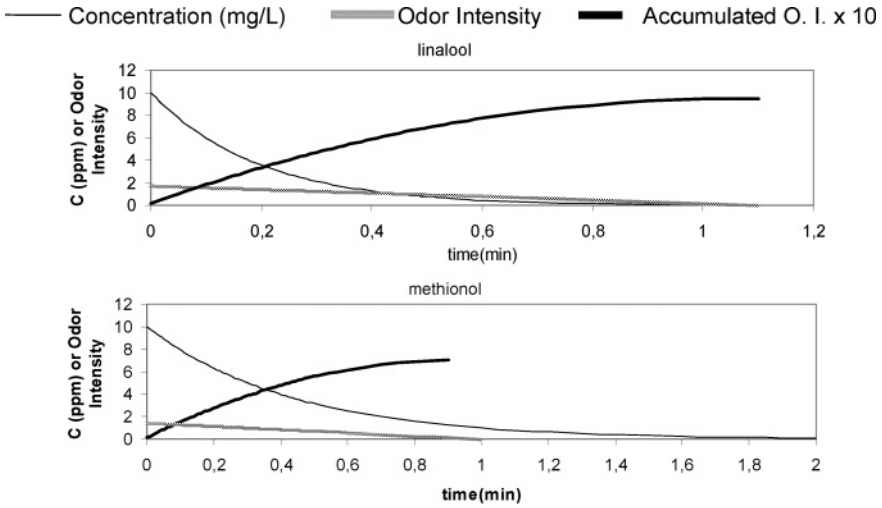

Figure 5. Evolution of concentration, odor intensity, and accumulated odor intensities (AOI) with time for two solutions containing 10 mg L^{-1} of linalool or methionol.

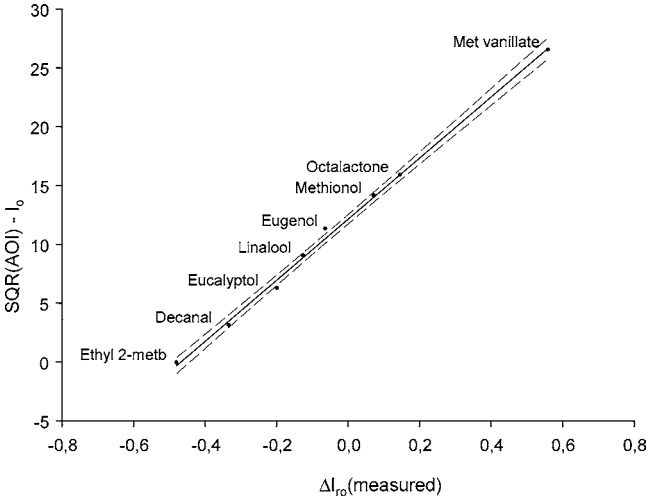

Figure 6. Differences between average retronasal (I_r) and orthonasal intensities (I_o), ΔI_{ro}, as a function of the predicted differences between square root of AOI and orthonasal intensities (averaged).

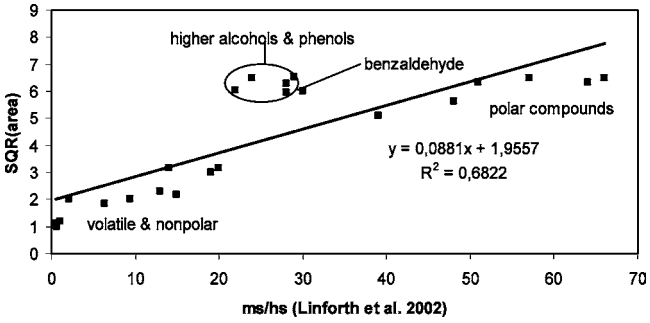

Figure 7. Regression plot of the data predicted by the model and the original mouthspace/headespace data presented by Linforth et al. (*12*).

which geometrically is the height of a square with such area, is proportional to the retronasal intensity of the compound.

For each of the eight studied compounds, the AOIs for each of the three solutions tested were calculated and averaged, giving a single value per compound. Then, the square root of such figure was taken, and the average orthonasal intensities obtained in the three solutions were subtracted. This parameter is closely related to the measured differences in intensity between retronasal and orthonasal olfaction, as can be seen in **Figure 6** ($R^2 = 0.99$, $F = 1989.7$, $P < 0.001$).

AOIs can also be used for the calculation of persistence. The olfactometric area is correlated (except in the case of methyl vanillate) with the experimental measurements of persistence ($R^2 = 0.85$, $F = 106.7$, $P < 0.001$).

Application of the Model to Data Presented by Other Authors. The model has been applied to part of the datasets presented by Linforth and Taylor and Linforth and colleagues in 2000 and 2002, respectively. In particular, the 23 components common to both datasets and for which persistence (instrumentally measured) and ms/hs or ns/hs data exist were selected. As a measure of volatility, Henry's constant has been used without any other transformation than a multiplication by 10000, to make its magnitude similar to that of K_{pm}. In this case, the accumulated concentration, instead of the AOI, has been recorded. Results of the study are shown in **Figures 7** and **8**. As both figures show, the square roots of the accumulated concentration (or area) are closely related to the instrumental measurements of persistence or ms/hs. In both cases, the relationship is linear and the square correlation coefficient is close to those originally found by the authors with log P or log K_{aw}. These results demonstrate that the proposed model is general and that it satisfactorily explains the role of volatility, measured now by K_H or K_{aw} and not by their log values.

In the case of **Figure 7**, a group of compounds behaves differently from expected according to the model, because their SQR(areas) are higher than those predicted. Surprisingly, all of these compounds share important chemical features, because they all have a relatively high molecular weight and a hydrogen atom with Lewis acid properties. It is not clear whether this particular behavior means that Henry's constant is not adequate to evaluate the volatility of these compounds in aqueous media (the volatility would be overestimated) or, on the contrary, that these compounds are more retained or absorbed by mucosa, which would cause an additional decrease of their concentration in the mouthspace. For nosepace/headspace values the plot is absolutely equivalent (plot not shown).

DISCUSSION

The proposed model differs in several key aspects from other models recently presented in the literature (*21*−*24*). A major difference is the objective. Most of the proposed models pursue a detailed explanation of the patterns of instrumental data obtained by MS-nose analysis. These data are collected continuously, which makes it possible to detect not only the general but also the fine details of the patterns. Accordingly, the models tend to include a large number of parameters and particular experimental details. In our case, we are modeling a sensory attribute, which is the result of a large number of transformations of the original signals, and there is no point in introducing many particular parameters. Second, in most cases the in vivo measurement involves extremely rigid protocols to control variability (*23*). One of the consequences of such procedures is

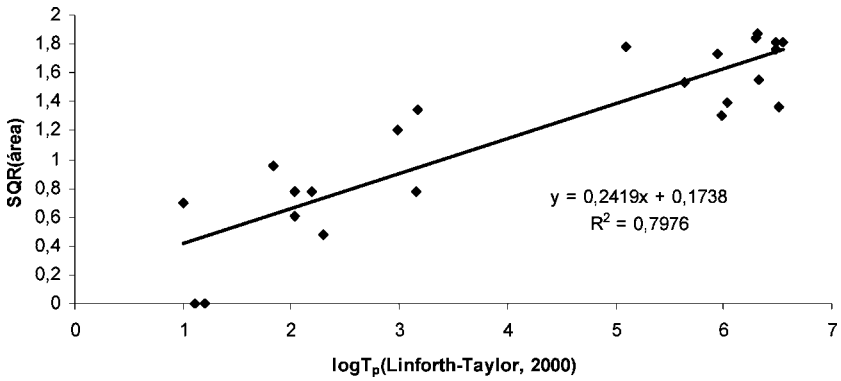

Figure 8. Regression plot of the data predicted by the model and the logarithm of the instrumental persistence (percent) data presented by Linforth and Taylor (*11*).

that the subjects are not allowed to freely swallow, which is not a real situation, although it makes the recordings more reproducible. Therefore, most of these models are exclusively considering the transference of odorants from the film deposited after the first swallowing in the throat, deliberately forgetting that the mouth is a more stable pool of odorants, as has been shown by Buettner (*14*) and Hodgson et al. (*25*), among others. Third, we are interested mainly in assessing the role of the volatility of the compound on the relative intensities of its different perceptual routes and on its persistence. This issue has not been satisfactorily solved by those models (mainly because they were not designed for such an aim). In fact, as stated in the Introduction, all of the relationships between the experimental measurements of persistence are with logarithms of volatilities and not with volatilities. Furthermore, there is a common agreement between researchers that large differences in volatility in vitro cause only small differences in apparent volatility in vivo (*23*, *25*). This question is partially answered with our model.

Volatility appears to be the main driving force of the release and transference of odorants from liquid solutions to the olfactory epithelium. Deliberately, the model does not consider any other parameter, such as interactions with mucosa (*26*) or with salivary proteins (*27*). Therefore, whenever such factors exert a significant effect, the model will fail, or, vice versa, whenever the model fails, it will be an indirect evidence of the existence of other effects.

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