

## Aroma Release from Wines under Dynamic Conditions

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Aroma release from wines and model ethanolic solutions during dynamic headspace dilution was measured in real time using atmospheric pressure chemical ionization–mass spectrometry. Model ethanolic solutions maintained the headspace concentration of volatile compounds close to equilibrium values during gas phase dilution over 10 min. Wine samples (with the same ethanol content) did not maintain the headspace concentration of volatiles to the same extent. Wine components and acidity ((+)-catechin, glycerol; pH 3.6) in model ethanolic solutions (120 mL/L) had no effect on the volatile headspace concentration during dynamic headspace dilution. However, in the presence of certain proteins ( $\beta$ -lactoglobulin,  $\beta$ -casein, bovine serum albumin), the model ethanolic solutions failed to maintain their volatile headspace concentration upon headspace dilution, but other proteins (thaumatin, mucin, lysozyme) had no effect. Thermal imaging of the model ethanolic samples (with and without  $\beta$ -casein) under dynamic headspace dilution conditions showed differences in surface temperatures. This observation suggested perturbation of the ethanol monolayer at the air–liquid interface and disruption of the Marangoni effect, which causes bulk convection within ethanolic solutions. Convection carries volatile compounds and warm liquid from the bulk phase to the air–liquid interface, thus replenishing the interfacial concentration and maintaining the gas phase concentration and interfacial surface temperature during headspace dilution. It is postulated that certain proteins may exert a similar effect in wine.

**KEYWORDS:** Marangoni; interfacial layer; surface active; protein; wine

### INTRODUCTION

Like many food products, the aroma character of wines is influenced by the volatile compounds that are present in the gas phase above the liquid and reach the receptors in the nose when the consumer is smelling the wine. Smelling a wine is a dynamic process, and aroma release is determined by the air–liquid partition ( $I$ ) basically influenced by the presence of ethanol, the presence of other solutes (2, 3), other physicochemical effects such as micelle formation (4), and surface tension effects (5).

Ethanol increases the solubility of volatiles (6) in the liquid phase and consequently decreases the headspace concentration. In model systems, the equilibrium headspace concentrations of volatile compounds above an ethanolic solution (120 mL/L) were decreased by <47% for 26 volatiles tested compared to water (6, 7). This decrease showed a parabola-like shape correlation with the hydrophobicity ( $\log P$ ) of the volatiles. Over a range of ethanol concentrations (0–230 mL/L), the effect of ethanol on the equilibrium headspace of volatiles was dependent on the volatile compound itself. However, as a general trend, the equilibrium headspace concentrations of volatiles decreased with an increase in ethanol concentration ( $I$ ). Other studies, however, demonstrated an effect of ethanol on the partitioning of compounds

only when the ethanol concentration in the solution was > 170 mL/L (8, 9).

Under dynamic conditions, when an inert gas diluted the equilibrium headspace above an ethanolic solution (120 mL/L), the headspace concentration of volatile compounds was maintained at levels close to that of the equilibrium headspace concentration. In contrast, the compounds in the headspace above aqueous solutions showed substantial headspace dilution ( $I$ ). This meant that after the first minute of headspace dilution, the absolute value of headspace concentration above an ethanolic solution 120 mL/L was higher than that above a water solution, even though in equilibrium headspace studies a decrease in headspace concentration of volatiles above ethanolic solutions compared with that above water solutions was mentioned ( $I$ , 7). It was suggested that ethanol in the solution improved mass transfer between the air and liquid phases (10), due to the surface tension differences of ethanol and water, which drive Marangoni convection ( $I$ ). Over a range of ethanol concentrations (0–230 mL/L), dynamic aroma release was dependent on the volatile. As a general trend, the dynamic headspace concentrations of volatiles above ethanolic solutions of 90–230 mL/L were similar to those obtained above a 120 mL/L solution. However, at 0–50 mL/L, dynamic headspace values were similar to those of aqueous samples, showing that there was a transition phase somewhere between 50 and 90 mL/L which was compound dependent ( $I$ ).

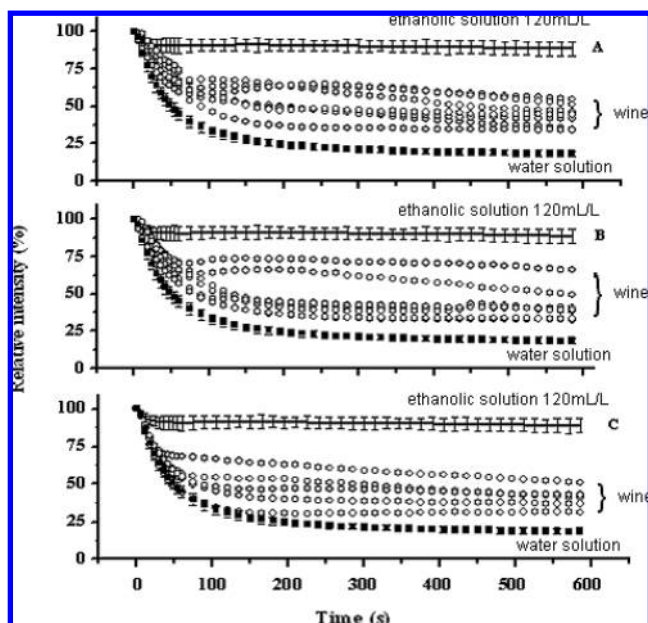
Wines typically contain between 100 and 145 mL/L, which places them in the zone where ethanol maintains the headspace

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**Table 1.** Variety and Origin of Wines Used in This Study, Wine Type, Year of Harvest, and Headspace Concentration of Volatiles at the End of the Dilution Process (10 min) Expressed as a Percentage of the Original Headspace Concentration (Ethanol Concentration of Wines in the Range of 120–135 mL/L)<sup>a</sup>

sample	year	1-octen-3-one	eucalyptol	ethyl 2-butenate	<i>p</i> -cymene
control: ethanol 120 mL/L		97 (±1);	97 (±2);	91 (±5);	12 (±1);
control: water		34 (±3);	30 (±3);	30 (±3);	0.9 (±0.4);
red wine <sup>b</sup>	2002	52 (±12);	60 (±10);	58 (±10)	9 (±2);
white wine <sup>c</sup>	2003	47 (±14)	57 (±10);	58 (±15);	4 (±2);
champagne <sup>d</sup>		44 (±9);	53 (±8)	54 (±7);	4 (±1);
champagne <sup>e</sup>		40 (±6);	53 (±12);	54 (±14);	4 (±2);

<sup>a</sup> Values are the mean of three to five replicates, with the standard deviation in parentheses. <sup>b</sup> Ruby Cabernet/California. <sup>c</sup> Chenin Blanc—Chardonnay/South Africa. <sup>d</sup> Pinot Noir—Pinot Meunier/Champagne. <sup>e</sup> Pinot Noir—Chardonnay/Champagne.



**Figure 1.** Relative headspace concentration of 1-octen-3-one, when an inert gas diluted the equilibrium headspace, above ethanolic solution 120 mL/L, water solution, and wines: (A) champagne/Pinot Noir—Pinot Meunier; (B) champagne/Pinot Noir—Chardonnay; (C) Ruby Cabernet. Points for ethanolic and water solutions are the mean of three replicates; error bars represent the standard deviation of the mean. S.D. was small and often cannot be seen over the size of the marker points. Points for wines represent experimental replicates.

concentration of volatiles close to their equilibrium headspace concentration. However, the presence of other solutes such as polyphenols, glycerol, and sugars may affect the aroma release. Dry red wines contain higher amounts of solutes compared to white wines and may show different dynamic aroma release profiles compared to model systems.

Dynamic headspace release studies allow real-time analysis of volatile headspace concentration above a solution as a flow of gas dilutes the equilibrium headspace. This can be achieved by real-time atmospheric pressure chemical ionization—mass spectrometry (APCI-MS) (11) or proton transfer reaction—mass spectrometry (12, 13). The APCI system was adapted to cope with the high amounts of ethanol found in the headspace of wine and ethanolic solutions while still monitoring the release of volatiles at much lower levels (about 10 mg/kg). Ethanol was introduced into the APCI-MS source makeup gas, so that ionization occurred under standard, stable conditions. The ionization of a wide variety of aroma compounds has been studied using ethanol as the reagent ion (6).

The aims of the current study were to investigate the aroma release above wines under dynamic conditions and to understand the effect of the presence of other solutes on volatile delivery from

the liquid to the gas phase as a step toward understanding the flavor release from wines and alcoholic beverages.

## MATERIALS AND METHODS

**Compounds.** Volatile solutions were prepared with the addition of eucalyptol (2.5  $\mu$ L/L), 1-octen-3-one (2.5  $\mu$ L/L), ethyl 2-butenate (0.5  $\mu$ L/L), and *p*-cymene (0.8  $\mu$ L/L) to (a) an ethanolic solution, 120 mL/L; (b) a water solution; and (c) wine, prior to analysis. All volatiles were obtained from Sigma-Aldrich (Gillingham, U.K.) and were of 97% purity or greater. Ethanol (analytical reagent grade, 99.99%) was purchased from Fisher Scientific (Loughborough, U.K.).

**APCI-MS.** A Platform LCZ mass spectrometer, fitted with an MS Nose interface (Micromass, Manchester, U.K.), sampled the headspace above the solutions (11). The APCI-MS source was operated with a modification as described previously (6), in which ethanol was added to the nitrogen makeup gas in a range of 2.0–11.3  $\mu$ L/L  $N_2$ , depending on the ethanol concentration of the sample. This was to ensure that the final concentration of ethanol in the source was the same whatever the ethanol concentration of the sample. The ethanol trimer ( $m/z$  139) was monitored in every experiment to ensure a consistent concentration of ethanol in the source (the ethanol monomer and the dimer ions were above the detection limits). Headspace was sampled into the mass spectrometer via a heated transfer line (120 °C) at 5 mL/min. Ions were monitored in full-scan mode at 1 scan/s ( $m/z$  30–350) with a cone voltage of 18 V or in selected ion mode with a specific cone voltage for each ion. The optimal cone voltages (V) for selected ion APCI-MS analysis were as follows: eucalyptol, 12; 1-octen-3-one, 21; ethyl 2-butenate, 21; *p*-cymene, 24 (dwell time = 0.5 s).

**Static Headspace Analysis.** Volatile solutions (40 mL) were placed in Duran graduated laboratory bottles (nominal size = 100 mL, real volume = 123 mL) (Sigma-Aldrich, Poole, U.K.) fitted with a one-port lid. After equilibration for at least 2 h at ambient temperature (22 °C), headspace was sampled through the port into the APCI-MS.

**Dynamic Headspace Dilution.** Volatile solutions (100 mL) were placed in Duran graduated laboratory bottles (nominal size = 100 mL, real volume = 123 mL), fitted with a two-port lid. After equilibration,  $N_2$  was introduced through one port (70 mL/min) to dilute the headspace. Steady flow was achieved by the use of a fine adjustment flow device including a flow meter, a flow calibration stopcock, and a flow valve. As the gas flowed out of the second port, part of the gas flow was sampled into the APCI-MS over a 10 min period (1). The profiles were normalized to the signal intensity at the start of the time course (100%).

**Wines.** Wines used in scan mode were (type/grape variety/wine region): red/Ruby Cabernet/California; white/Chenin Blanc—Chardonnay/South Africa; champagne/Pinot Noir—Pinot Meunier/Champagne; champagne/Pinot Noir—Chardonnay/Champagne. Champagne wines were degassed prior to analysis.

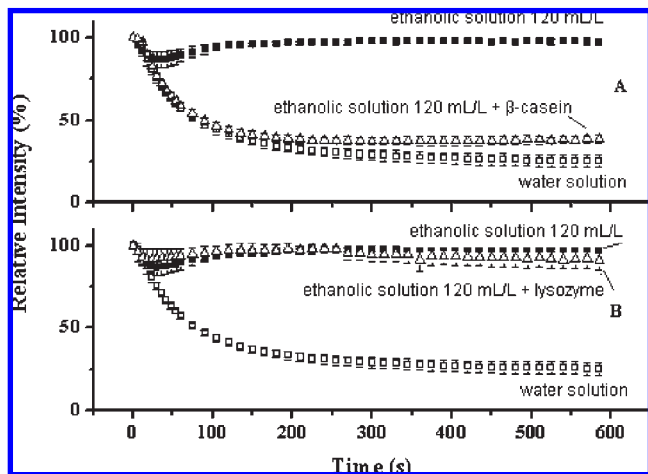
**Wine Dilution.** Ruby Cabernet/California red wine was diluted with an ethanolic solution of the same ethanol strength (135 mL/L) to final dilutions of 20, 40, 60, 80, and 100% wine in ethanolic solution. A pure ethanolic solution of 135 mL/L was used as control. Volatiles were added to each solution.

**Effect of pH, Catechin, and Glycerol.** Glycerol, 7 g/L; (+)-catechin, 450 mg/L; and 10 mM sodium tartrate buffer (pH 3.6) were obtained from Sigma-Aldrich and added separately and in combination to an ethanolic solution (120 mL/L). Volatiles were added to each solution. Each solute was tested in three to five replicates.

**Table 2.** Headspace Concentration of Volatiles at the End of the Dilution Process Relative to Equilibrium Headspace Concentration above a Wine<sup>a</sup> at Different Dilutions

wine percentage <sup>b</sup> (%)	1-octen-3-one	eucalyptol	ethyl 2-butenate	<i>p</i> -cymene
control: ethanol 120 mL/L	97 (±1);	97 (±2);	91 (±5);	12 (±1);
control: water	34 (±3);	30 (±3);	30 (±3);	0.9 (±0.4);
20	55 (±19) <sup>c</sup>	62 (±17) <sup>c</sup>	58 (±15) <sup>c</sup>	6 (±3) <sup>c</sup>
40	68 (±12) <sup>c</sup>	76 (±10) <sup>c</sup>	71 (±12) <sup>c</sup>	11 (±3) <sup>c</sup>
60	51 (±12) <sup>c</sup>	61 (±10) <sup>c</sup>	57 (±9) <sup>c</sup>	8 (±3) <sup>c</sup>
80	47 (±6) <sup>c</sup>	57 (±4) <sup>c</sup>	53 (±6) <sup>c</sup>	6 (±2) <sup>c</sup>
100	52 (±12) <sup>c</sup>	60 (±10) <sup>c</sup>	58 (±10) <sup>c</sup>	9 (±2) <sup>c</sup>

<sup>a</sup> Wine used for the study: red, 2002, Ruby Cabernet/California. Values are the mean of three replicates with the standard deviation in parentheses. <sup>b</sup> Percentage of wine used in a solution of the same ethanol strength. <sup>c</sup> Denotes no significant difference from the value of the 100% wine, for each volatile.



**Figure 2.** Dynamic headspace concentration profile of 1-octen-3-one above an ethanolic solution 120 mL/L: a water solution and an ethanolic solution 120 mL/L containing  $\beta$ -casein (A) and lysozyme (B). Points represent the mean of five replicates; error bars represent the standard deviation of the mean. S.D. was small and often cannot be seen over the size of the marker points.

**Protein Solutions.** Lysozyme, 50 mg/L;  $\beta$ -casein, 5 mg/L; bovine serum albumin, 50 mg/L;  $\beta$ -lactoglobulin, 50 mg/L; thaumatin, 50 mg/L; and mucin, 50 mg/L, were added separately to water and ethanolic solutions, 120 mL/L, containing volatiles as above. The proteins were tested in solutions adjusted to pH 3.0 ( $\pm 0.05$ ). Proteins were obtained from Sigma-Aldrich. Statistical analysis was carried out with SPSS 12.0.1 for Windows, SPSS Inc.

**Thermal Imaging Analysis.** Thermal imaging analysis of an ethanolic solution (120 mL/L) with and without 50 mg/L  $\beta$ -casein used an Agema Thermovision 900 (Agema Infrared Systems, Sweden; currently Flir Systems, Boston, MA) thermal imaging camera (wavelength range of 8–12  $\mu$ m, mercury–cadmium–telluride detector). Two Duran borosilicate glass Schott bottles were used (nominal size = 100 mL), which are opaque to IR radiation (14). These were filled to the top with liquid (diameter of the opening of the top = 2.95 cm) and placed 45 cm below the thermal imaging camera. An air flow ( $2.06 \times 10^{-5}$  m<sup>3</sup>/s) was generated parallel to the top of the two flasks. The first image was taken at 0 s, and then the air stream was turned on and images were taken every 30 s for a 7 min period. All of the solutions tested and flasks used were kept in a water bath (set at 20 °C) prior to the experiment for at least 2 h to ensure uniformity of sample temperature.

## RESULTS AND DISCUSSION

**Scan Analysis of Wines by APCI-MS.** The equilibrium headspace above four different wines was analyzed in full-scan mode ( $m/z$  30–350) by APCI-MS. Ions  $m/z$  89 and 135 were the most abundant species, but the intensities of all other ions were about 10 times less. The purpose of this scan was to find  $m/z$  values

where the ion abundance was low and then to choose volatile compounds that were known to form ions at these masses to act as markers of volatile behavior in a wine matrix. The compounds selected as markers in wine were eucalyptol ( $m/z$  155), 1-octen-3-one ( $m/z$  127), ethyl 2-butenate ( $m/z$  115), and *p*-cymene ( $m/z$  134). These volatiles were also chosen because of their different physicochemical properties (15). Volatiles spiked into the wine were expected to behave in the same way as volatiles naturally present in the wine with similar physicochemical properties.

**Dynamic Aroma Release from Wines.** Model ethanolic solutions maintained their headspace concentration under dynamic headspace dilution conditions when ethanol concentrations were > 60 mL/L (1), so similar aroma release behavior might be expected from wines. The wines were spiked with the marker compounds and analyzed by dynamic headspace dilution. For the majority of the wines tested, the headspace concentration of volatiles depleted significantly under dynamic conditions (Table 1) in contrast to model ethanolic solutions. The dynamic headspace concentration of 1-octen-3-one at the end of the dilution process varied from 30 to 52% of the initial concentration for the wines tested, whereas ethanolic solutions maintained headspace at 97% of initial value (Figure 1). The dynamic headspace concentration of volatiles did not seem to follow any specific trend depending on the type of wine. The results of dynamic headspace analysis above wines also showed a much higher variation compared to the controls (Figure 1 and Table 1). The other marker compounds also showed the same effect (Table 1); the headspace volatile concentration during dilution was intermediate between that of the water and ethanol solution controls, and the data for the wines were more variable than that of the controls.

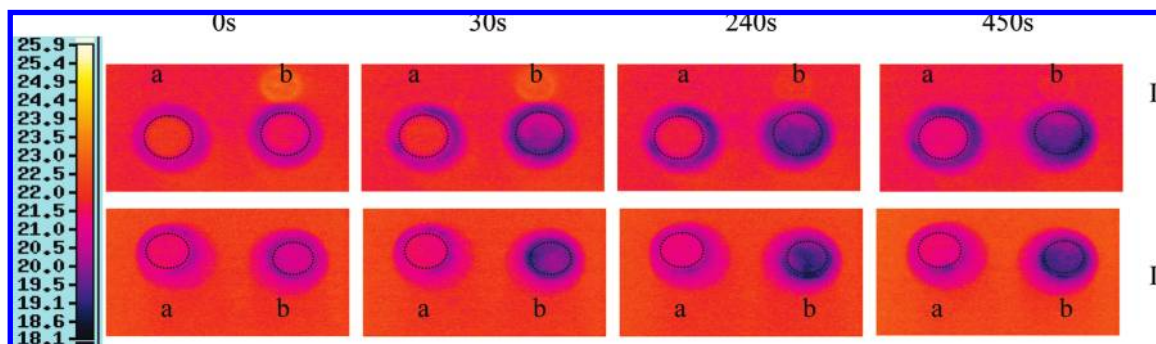
**Effect of Wine Dilution on Aroma Release from Wines.** The majority of the wine solutes are present in wine at very low concentrations; therefore, it is not clear if they could have an effect on dynamic aroma release. One approach to study them collectively was to see if the differences between wine and an ethanolic solution could be eliminated by dilution to reduce the solute concentration.

A wine for which the dynamic aroma release profile was significantly different from the ethanolic control (Table 1, Ruby Cabernet/California) was diluted with an ethanolic solution of the same ethanol strength. As expected, the equilibrium headspace concentration decreased with dilution (data not shown), but the relative decrease in dynamic headspace concentration at different wine dilutions still showed significant headspace depletion compared to the ethanolic solution (Table 2). Moreover, the dilutions still showed high variation (as in the case of 100% wine), with the %CV (standard deviation  $\times$  100/mean) varying from 6 to 19% for 1-octen-3-one. The same was true for the other volatiles. Therefore, the wine solutes responsible for the dynamic aroma release profile above wine could affect the behavior even

**Table 3.** Headspace Concentration of Volatiles at the End of the Dilution Process Expressed as a Percentage of Equilibrium Headspace Concentration above an Ethanolic Solution (120 mL/L) Containing Different Proteins<sup>a</sup>

protein <sup>b</sup>	1-octen-3-one	eucalyptol	ethyl 2-butenate	<i>p</i> -cymene
control: ethanol (120 mL/L)	97 (±1);	97 (±2);	91 (±5);	12 (±1);
control: water	34 (±3);	30 (±3);	30 (±3);	0.9 (±0.4);
bovine serum albumin	37 (±2);	47 (±2);	43 (±2);	2 (±0.3);
$\beta$ -lactoglobulin	36 (±2);	48 (±3);	41 (±3);	2 (±0.3);
$\beta$ -casein	38 (±3);	49 (±4);	44 (±3);	2 (±0.2);
lysozyme	91 (±6);	94 (±4);	92 (±5);	16 (±2);
thauMATIN	81 (±11);	86 (±8);	77 (±7);	10 (±2);
mucin	91 (±5)	93 (±4);	86 (±4);	11 (±2);

<sup>a</sup> Values are the mean of five replicates, with the standard deviation in parentheses. <sup>b</sup> Protein concentration was 50 mg/L apart from  $\beta$ -casein, which was 5 mg/L; all protein solutions were adjusted to pH 3 (±0.05) with a 10 mM sodium tartrate buffer.



**Figure 3.** IR images of the top of Schott flasks (volume = 123 mL) at 0, 30, 240, and 450 s of air flow blowing at  $1.24 \times 10^{-3} \text{ m}^3/\text{min}$  parallel to the surface of the liquid from a distance of 0.7 m. The scale on the left-hand side shows the color–temperature ( $^{\circ}\text{C}$ ) relationship. Samples: I-a and II-a, ethanolic solution 120 mL/L; I-b, ethanolic solution 120 mL/L with  $\beta$ -casein; II-b aqueous solution (images of panel II first appeared in ref 10).

after a 5 times dilution of wine. Further investigation of the aroma release from wines was performed to study the influence of different wine solutes.

**Effect of pH, Catechin, and Glycerol on Aroma Release from Ethanolic Solutions.** To investigate why aroma release from wines presented a very different profile from model ethanolic solutions, the effect of different wine solutes in model ethanolic solutions was studied. Glycerol and catechin represent two important wine solutes in terms of their concentration. pH is also one of the most significant parameters defining the nature of the wine medium. pH was not found to have any significant effect on the equilibrium headspace concentration of volatiles (16), but no studies on dynamic aroma release have been reported.

The presence of catechin, glycerol, and low pH had no effect whatsoever on dynamic aroma release from ethanolic solutions (120 mL/L). The relative headspace concentration of 1-octen-3-one at the end of the dilution process above an ethanolic solution 120 mL/L, containing separately catechin, glycerol, or sodium tartrate buffer (pH 3.6), was not significantly different from that above the control ethanolic solution. The same was true when these systems were used in combination. Similar results were obtained for the other volatile molecules tested (data not shown).

The ability of volatiles to maintain their headspace concentration above ethanolic solutions is related to the interfacial properties of ethanol and the bulk convection forces created (1). These convection forces, known as Marangoni convection, involve the transport of material from the bulk liquid phase to the interface through motions energized by surface tension gradients, providing a better mass transfer of volatiles due to the convective forces created (19). Molecules that might disturb this behavior would need to compete with ethanol for sites at the air–liquid interface and thereby disturb the mechanism by which ethanol “replenished” the interface. However, neither the solutes tested nor low

pH altered the dynamic headspace behavior and, by extrapolation, the ethanol interfacial behavior. Therefore, other molecules found in wine should be considered as possible candidates causing the different dynamic aroma release profile above wines compared to ethanolic solution (120 mL/L).

**Effect of Proteins on Aroma Release from Ethanolic Solutions.** It has been demonstrated that different macromolecules and especially proteins have a tendency to adsorb at the air–wine interface and lower the surface tension (17). Indeed, some proteins are highly surface active molecules. In wines they are present in very low concentrations, 10–230 mg/L. Under equilibrium conditions, the relative headspace concentration of volatiles showed no significant differences between the control solutions and the sample solutions containing proteins ( $P > 0.05$ ). This suggested no significant binding between the volatiles and the proteins.

The effect of different proteins on the dynamic headspace concentration of volatiles above ethanolic solution (120 mL/L) was investigated. The dynamic headspace concentration of 1-octen-3-one above an ethanolic solution containing  $\beta$ -casein decreased readily upon dilution to 38% of the initial concentration prior to dilution (Figure 2; Table 3), showing a behavior very close to that of an aqueous solution. The same was also true for the dynamic headspace concentration of 1-octen-3-one above an ethanolic solution containing  $\beta$ -lactoglobulin and bovine serum albumin (1-octen-3-one headspace concentration at the end of the dilution process at 36 and 37%, respectively). The same decrease of the dynamic headspace concentration at the end of the dilution process was also seen for the other volatiles. Eucalyptol dynamic headspace concentrations at the end of the dilution process were 47, 48, and 49% of the initial headspace concentration, prior to dilution, when bovine serum albumin,  $\beta$ -lactoglobulin, and  $\beta$ -casein were present in the ethanolic solution (120 mL/L), respectively (Table 3). Ethyl 2-butenate showed analogous

results (Table 3). The dynamic headspace concentration of *p*-cymene above an ethanolic solution (120 mL/L) containing bovine serum albumin,  $\beta$ -lactoglobulin, and  $\beta$ -casein was at 2% of the initial headspace concentration prior to dilution. *p*-Cymene headspace concentration above an ethanolic solution of 120 mL/L showed a considerable decrease upon dilution, reaching 12% of the initial headspace concentration prior to dilution (Table 3), due to its air–water partition coefficient  $K_{aw}$  ( $4.05 \times 10^{-1}$ ) (1). Therefore, *p*-cymene headspace concentration at the end of the dilution process also showed a decrease in the presence of protein compared with the ethanolic control. A similar mechanism may account for the behavior of all four compounds.

$\beta$ -Casein and bovine serum albumin are reported to adsorb at the interface of an aqueous–ethanol solution soon after a fresh air–liquid interface is created (18). It could be suggested that their adsorption at the interface disturbed the continuity of the interfacial arrangement of ethanol molecules. This could strongly interfere with the Marangoni convection mechanism, and hence the headspace concentration of the volatiles depleted considerably upon dilution. The same could be assumed for  $\beta$ -lactoglobulin.

However, not all of the proteins had this effect on the headspace concentration of the volatiles upon dilution. The dynamic headspace concentration of the four volatiles above ethanolic solutions containing lysozyme did not decrease upon dilution (Figure 2; Table 3); this was also true for ethanolic solutions containing thaumatin and mucin. The results for lysozyme were consistent with the fact that lysozyme has an almost negative adsorption at an air–water interface for the first 60 min after forming a fresh air–liquid interface (18). Consequently, the ethanol arrangement at the interface remained undisturbed for the whole duration of the current experiment. Volatile molecules were still transported to the interface according to the Marangoni convection mechanism. Even though it is not clear if the same mechanism, of slow adsorption to interface, was applicable when thaumatin and mucin were in the solution, it was obvious that their presence in the solution did not affect the dynamic release of volatiles from the liquid for the duration of the experiment.

**Thermal Imaging Studies.** To study the behavior of the interface in the presence and absence of proteins, thermal imaging was used to monitor the temperature of the interface during dynamic headspace dilution. The hypothesis was that solutions that maintained their headspace concentration of volatiles under dynamic conditions should be undergoing Marangoni convection and that this mechanism would “stir” the bulk phase and minimize localized interfacial cooling due to the evaporation of ethanol. In contrast, if ethanol evaporation from the interface was inhibited by the presence of proteins, the Marangoni process would not occur and the surface layer would not be readily replenished, leading to a decrease in surface temperature by ethanol evaporation. Comparisons were made between ethanolic and aqueous solutions with and without protein ( $\beta$ -casein).

The ethanolic solution without  $\beta$ -casein showed little change in liquid surface temperature, whereas the ethanolic solution with  $\beta$ -casein showed a significant decrease with time (Figure 3) as did the thermal images from the aqueous solution. Thus, the results support the hypothesis that  $\beta$ -casein interferes with ethanol at the air–liquid interface.

Therefore, dynamic aroma release from wines is very different from that from model ethanolic solutions. Catechin, glycerol, and pH were not responsible for the different behavior, but certain proteins changed the dynamic release profile from “ethanol-like” to “water-like”. The spiked wine samples showed dynamic release profiles that were intermediate between those of ethanol and

water systems. The replicates were more variable than the model systems, maybe reflecting the dynamic state of wine.

Further investigation is needed to fully understand the influence of wine proteins on their dynamic aroma release profiles. It is well-known that the aroma profile of aged red wines improves, and it may be caused by the absence of proteins in the liquid, as the majority of proteins precipitate in complexes with tannins over time. Furthermore, the effect of other surface active molecules originated from the wine or transferred to it from the glass (soaps, lipids from food, etc.) may be another significant factor affecting the aroma profile above wine and other alcoholic beverages.

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