

## Which Impact for $\beta$ -Damascenone on Red Wines Aroma?

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$\beta$ -Damascenone, a C-13 norisoprenoid compound, is usually presented as an impact odorant in red wines. Its direct contribution to their aroma was investigated. Both free  $\beta$ -damascenone and  $\beta$ -damascenone precursors were isolated from various French red wines and then analyzed by gas chromatography–mass spectrometry, revealing concentrations in the vicinity of 1 and 2  $\mu\text{g/L}$  for free compounds and both forms, respectively. Gas chromatography–olfactometry analyses were also performed on dilutions of both red wine extracts and pure  $\beta$ -damascenone. The very low detection threshold in olfactometry for this compound explains why it is found at the highest dilution factor in aroma extract dilution analysis methods. Moreover, determination of  $\beta$ -damascenone's odor thresholds confirmed the huge importance of the matrix:  $\beta$ -Damascenone is characterized by a very low perception threshold in hydroalcoholic solution as compared to red wine, where it is over 1000-fold higher. In hydroalcoholic solution,  $\beta$ -damascenone enhanced fruity notes of ethyl cinnamate and caproate and masked the herbaceous aroma of IBMP. Globally, these results suggested that  $\beta$ -damascenone has more an indirect than a direct impact on red wine aroma.

**KEYWORDS:** Red wine;  $\beta$ -damascenone; odor threshold; matrix; aromatic interactions

### INTRODUCTION

Over the past 20 years, research into specific impact odorants in red wines has highlighted the possible importance of C13-norisoprenoid compounds, especially  $\beta$ -damascenone. This compound, first isolated from Bulgarian rose oil by Demole et al. (1) and from grapes and wine by Schreier et al. (2), was identified as a key odor in various fruits (peaches, lychees, and grapes) and beverages (coffee, beer, and wine), generally associated with descriptors such as “fruity-flowery” (3, 4), “woody” (3, 5), “honey-like” (6), and especially “apple” (5, 7) and “baked apple” (8).

$\beta$ -Damascenone is generated from multiple grape glycoconjugated precursors, involving different conjugated moieties, as well as polyols (9, 10). For example,  $\beta$ -damascenone can be formed by acid-catalyzed conversion of megastigma-6,7-diene-3,5,9-triol and megastigma-5-ene-7-yne-3,9-diol, derived from enzymatic transformations of the carotenoid, lutein (11, 12).

$\beta$ -Damascenone in free form or bound to glucose has different chemical properties. In fact, free forms are characterized by their volatility and hydrophobia, while bound forms are both soluble and nonvolatile (13).

In studies of red wine aromas, even those only partially concerned with C13-norisoprenoids,  $\beta$ -damascenone is the most

frequently mentioned compound. Lopez et al. (14) revealed that  $\beta$ -damascenone was one of the odorants present in every wine analyzed by gas chromatography–mass spectrometry–olfactometry (GC-MS-O). It was also consistently perceived at the highest dilution factor (FD) in aroma extract dilution analysis (AEDA).  $\beta$ -Damascenone was also one of the few odorants perceived at the highest FD in extracts of Merlot and Cabernet Sauvignon wines (8), as well as Rioja extracts (5).  $\beta$ -Damascenone has thus clearly been established as a key odorant in red wine extracts.

In the literature,  $\beta$ -damascenone is characterized by a great diversity of odor thresholds, depending on the matrix used. All sources agree on an extremely low odor threshold in water: 2–9 ng/L (13, 15), with 2 ng/L most often used as a reference value (16). Its odor threshold in hydroalcoholic solution (10–12%, v/v, water/ethanol mixture) is also very low, approximately 50 ng/L (16–18), while values in wine vary considerably, ranging from 4 (19) to about 7  $\mu\text{g/L}$  (8, 20). In sweet white wine, Etievant et al. (21) estimated the threshold at 4.5  $\mu\text{g/L}$ . Thus, according to previous research, we can only have an idea of  $\beta$ -damascenone perception threshold in red wine. Till now, no consensus exists on an average value that could be seen as a reference.

The  $\beta$ -damascenone content of various wines was evaluated. In Merlot Noir wines, concentrations were between 250 and 1300 ng/L (22). In Grenache wines, values varied from 1000 to 4000 ng/L (19). Determinations in 57 oak-aged Spanish wines found an average concentration of 1500 ng/L, with values

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**Table 1.** Free  $\beta$ -Damascenone,  $\beta$ -Damascenone Precursors and Total  $\beta$ -Damascenone Concentrations in ng/L Obtained by GC-MS

origin	vintage	varieties	free $\beta$ -damascenone	$\beta$ -damascenone precursors	total
Bordeaux	2002	Merlot	1042	1933	2975
	2002		1070	1781	2851
	2002		787	1458	2245
	2002		1356	914	2270
	2002	Cabernet Franc	1357	1317	2674
	2002		977	943	1920
	2002	Cabernet Sauvignon	1367	1001	2368
	2002		1711	1328	3039
Rhône	2002	Grenache, Syrah, Mourvèdre	1560	551	2111
	2002		545	705	1250
	2001		714	149	863
Burgundy	2002	Pinot Noir	471	448	919
	2002	Pinot Noir	242	367	609
Loire	2002	Gamay	845	264	1109
	2002		740	367	1107
	2002	Gamay	598	216	814
Provence	1999		745	660	1405
	2002		1042	823	1865
Languedoc/Roussillon	2001		2307	911	3218
	2001		801	912	1713
	2002		593	606	1199
	2002	Merlot	1092	254	1346

ranging from 320 to 3400 ng/L (18). Generally, the  $\beta$ -damascenone content of red wine is around 1–1.5  $\mu$ g/L.

Authors often explain the contribution of  $\beta$ -damascenone to wine aroma by its odor activity value (OAV), defined as the ratio of a wine's  $\beta$ -damascenone content over its perception threshold in water or hydroalcoholic solution (23).  $\beta$ -Damascenone is considered to have a very high OAV, indicative of its major contribution to wine aroma.

The goal of our study was to determine the real influence of  $\beta$ -damascenone on red wine aroma. Was it possible to link GC-O analyses, indicating that  $\beta$ -damascenone had a major impact on aroma in wine extracts, with sensorial and organoleptic analyses? The aim was to determine whether the role of  $\beta$ -damascenone in wine extract was representative of its real contribution to wine aroma. Otherwise, what exactly was the role of  $\beta$ -damascenone in red wines aroma?

## MATERIALS AND METHODS

**Wines Analyzed.** Nine red wines representative of the Bordeaux region's diversity of soils and grape varieties were used in this study, that is, single-varietal wines from *Vitis vinifera* L. var. Merlot, Cabernet Sauvignon, and Cabernet Franc, cultivated on three different soils: gravel, clay, and sand. Physical characteristics of these soils are described by Van Leeuwen et al. (24). All wines analyzed were from the 2002 vintage. Fourteen other wines, representative of the diversity of red varieties grown in France, were also analyzed. Their characteristics are listed in Table 1.

**Chemicals and Solvents.** All of the chemicals and solvents used were of analytical quality. Diethyl ether, ethanol, and hexane were purchased from VWR (Fontenay-sous-bois, France).  $\beta$ -Damascenone was obtained from Fluka (Buchs, Switzerland), while ethyl-4-acetylbenzoate, ethyl caproate, and 2-isobutyl-3-methoxypyrazine came from Aldrich (St. Louis, MO). XAD-2 (Amberlite) apolar resin was from Supelco (Bellefonte, United States). Microfiltered water (resistivity, 18.2 M $\Omega$  cm) was used.

**Quantification of  $\beta$ -Damascenone in Wines.** To extract free  $\beta$ -damascenone, 50 mL of wine was supplemented with 50  $\mu$ L of ethyl-4-acetylbenzoate in aqueous alcoholic solution (1/1, v/v) at 0.91 mg/L as an internal standard. The wine was extracted at room temperature, using 4, 2, and 2 mL of diethylether/hexane (1:1, v:v), with magnetic stirring (2000 rpm) for 5 min. The three extracts were blended (5–6 mL of total extract) and dried over anhydrous sodium sulfate,

concentrated 10-fold under a nitrogen stream (1 L/min), and maintained at  $-20$  °C until analysis.

The quantification of  $\beta$ -damascenone precursors was assayed as described by Günata et al. (25). After isolation of the volatiles by liquid–liquid extraction (free  $\beta$ -damascenone extraction method), any trace of solvent was eliminated from the wine sample using a Rotavapor for 10–15 min (bath temperature, 25 °C).

Isolation of  $\beta$ -damascenone precursors was then performed by a solid–liquid extraction on XAD-2 resin (Amberlite). Nine milliliters of resin was put in a column (internal diameter, 1.5 cm; length, 20 cm) and conditioned successively with 60 mL of methanol, 60 mL of diethylether, and 60 mL of Millipore MilliQ water. The wine sample was then loaded, followed by 120 mL of distilled water. Precursors were finally eluted from the resin with 50 mL of methanol (all liquids were loaded at a flow rate of about 2.5 mL/min). The methanol extract was evaporated to dryness using a Rotavapor (bath temperature, 25 °C). The residue was taken up in 20 mL of a citric acid buffer (0.1 N), sealed under nitrogen atmosphere in a 25 mL glass ampule, and hydrolyzed at 100 °C for 1 h to generate hydrolytically released  $\beta$ -damascenone.

After the mixture was cooled, 24 mL of Millipore MilliQ water and 6 mL of ethanol were added to restore a 50 mL sample, from which hydrolytically released  $\beta$ -damascenone was extracted using the free  $\beta$ -damascenone extraction method.

Two microliters of extract was then injected into the GC with an MS detector. Chromatographic conditions were as follows: Hewlett-Packard HP 6890 gas chromatograph coupled with a mass spectrometer (HP 5973); electron impact, 70 eV; selected ion monitoring (SIM) detection mode with  $m/z$  121 (internal standard and  $\beta$ -damascenone quantification) and  $m/z$  177 ( $\beta$ -damascenone qualification) ions; BP20 (SGE) column, 50 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness; helium 5.6 Aga pressure, 55 kPa; injector temperature, 220 °C; detector temperature, 250 °C; oven temperature, 40 °C for 1 min programmed at a rate of 3 °C/min to 230 °C, the final step lasting 15 min; splitless time, 30 s; and split flow, 30 mL/min.

Intralaboratory repeatability was determined by 10 successive analyses of the same red wine containing 400 ng/L  $\beta$ -damascenone, and the variation coefficient was 0.76%. It was quite similar to the 0.8% obtained with labeled [ $^2$ H $_4$ ] $\beta$ -damascenone by Kotsieridis et al. (3). The linearity of the method was evaluated by adding  $\beta$ -damascenone (0, 100, 200, 400, 800, 1600, and 3200 ng/L) to the same red wine initially containing 400 ng/L  $\beta$ -damascenone. The correlating coefficient between found and added levels was 0.9991.

**Table 2.** Matrices and Range of Concentrations Tested in  $\beta$ -Damascenone Odor Threshold Determinations

matrix	concentration range (in ng/L)
hydroalcoholic solution	20–40–60–80–100
model white wine	25–50–100–150–200
model red wine 1	100–200–300–400–700–1000–2000–3000
model red wine 2	75–100–200–300–400–700–1000–2000
red wine	2000–4000–6000–8000–10000

**GC-O Analyses.** GC-O analyses were carried out under the same conditions as the GC-MS analyses but with an initial temperature of 45 °C in the oven program and an olfactometric detection system. The make-up gas on the olfactometric device was air (80% N<sub>2</sub>; 20% O<sub>2</sub>) (Air Liquide, France). All GC-O analyses were performed by a panel of three trained judges.

**AEDA.** FDs for  $\beta$ -damascenone in wine extracts were determined by AEDA. Two microliters of concentrated extract used for quantification was separated on a capillary column, and the odor-active region for  $\beta$ -damascenone was evaluated by three different trained judges. The extracts were stepwise diluted with diethylether/hexane (1:1, v:v), and aliquots of the dilutions were evaluated by each of the same judges. The process stopped when  $\beta$ -damascenone was no longer detected. The same dilution method, applied to a pure  $\beta$ -damascenone solution in diethylether/hexane (1:1, v:v), was used to determine the minimum quantity of  $\beta$ -damascenone perceived under these analytical conditions.

**Determining Odor Thresholds.** The sensory panel consisted of about 50 students, who received weekly training sessions. Tests were performed at a controlled room temperature of 20 °C, in individual booths, using covered AFNOR (Association Française des Normes) glasses, containing about 40 mL of liquid. Olfactory odor thresholds were measured using ranking tests, with series of triangle tests presented following increasing  $\beta$ -damascenone content. In each triangle test, the jury tested three samples; one contained the target compound dissolved in the matrix, while the other two consisted of the matrix alone. In another triangle test, the presentation was reversed. Thresholds were determined from the analysis of individual thresholds of the judges. The individual odor threshold of each judge corresponded to the first concentration from which all of his triangular tests were valid. Compiling these results, a detection rate was calculated for each concentration tested: It corresponded to the percentage of judges whose individual odor threshold was inferior or equal to the concentration considered. A graph was then established with the detection rates obtained for each concentration. The  $\beta$ -damascenone odor threshold was finally determined extrapolating from this graph the  $\beta$ -damascenone concentration corresponding to a 50% perception rate of the judges. Four odor thresholds were determined for  $\beta$ -damascenone, each using an increasing range of five or eight concentrations in different matrices, as summarized in **Table 2**. The hydroalcoholic solution was a water/ethanol mixture (88:12, v:v), with 4 g/L tartaric acid, pH adjusted to 3.5 (0.5 N KOH). Model white wine was prepared by mixing 1 g of charcoal with 1 L of white wine (Chardonnay) for 48 h in a closed bottle. The mixture was then filtered to remove the charcoal, and the liquid was mixed with 1 g of charcoal for 24 h and then filtered. The second step was repeated as many times as necessary to obtain a model white wine without any traces of  $\beta$ -damascenone (i.e., below 2 ng/L). The whole operation was carried out under a nitrogen steam to avoid oxidizing the wine. From an aromatic point of view, the model white wine smelled very neutral, without any fruity aromas. The red wine was a Merlot from the Languedoc region, with a  $\beta$ -damascenone concentration evaluated at 400 ng/L. Concentrations used in ranking tests took the initial concentration into account. Two model red wines were obtained from the initial wine. Model red wine 1 was prepared by evaporating a red wine using a Rotavapor (Büchi, CH), with a 20 °C bath temperature. The viscous residue was washed with 25 mL of methanol and then evaporated again. That step was repeated twice. Finally, a water/ethanol (88:12, v:v) mixture was added to the residue to reconstitute the initial volume of wine. Model red wine 2 was prepared by a two-thirds evaporation of 1.5 L of red wine (the same wine used to prepare model red wine 1). The liquid was then mixed

with 180 mL of absolute ethanol, and finally, the mixture was diluted with MilliQ water to obtain 1.5 L. Analysis of model red wines 1 and 2 confirmed that the matrices contained no  $\beta$ -damascenone. From an aromatic point of view, model red wine 2 was neutral, while model red wine 1 presented caramel and candied fruit aromas.

Five ranking sessions were organized to test the indirect impact of  $\beta$ -damascenone on the odor thresholds of three aromatic compounds: ethyl cinnamate, ethyl caproate, and 3-isobutyl-2-methoxypyrazine. The odor thresholds were evaluated with and without 50 ng/L  $\beta$ -damascenone in model wine, as shown in **Table 3**.

## RESULTS AND DISCUSSION

**Table 4** shows the wide diversity of odor thresholds obtained. In agreement with previous studies (13, 16), the odor threshold of  $\beta$ -damascenone in hydroalcoholic solution was very low, only 50 ng/L, while it was three times higher in model white wine, 15–42 times higher in model red wine, and even 140 times higher (7  $\mu$ g/L) in red wine. The same kind of variation in odor threshold was previously reported by Kotseridis et al. for another C13-norisoprenoid compound in red wines (16). They demonstrated that the odor threshold varied, depending on the initial concentration of the compound in the matrix. Moreover, the values obtained in their experiments were “recognition thresholds”, which are usually higher than their corresponding “perception thresholds”. These authors indicated that it was extremely difficult to determine an odor threshold in a matrix that already contained the compound being tested. In that case, the odor threshold may be considered a maximum value, even though concentrations used in ranking tests took the initial concentration into account. The odor threshold (7  $\mu$ g/L) for the red wine that initially contained 400 ng/L  $\beta$ -damascenone was certainly overevaluated. In other words, the  $\beta$ -damascenone odor threshold in a red wine should be below 7  $\mu$ g/L. On the contrary, as the model base red and white wines contained no  $\beta$ -damascenone, they were far from representative of the original wines and could almost be regarded as hydroalcoholic solutions. This was particularly true of model white wine and model red wine 2, which were aromatically neutral. The odor thresholds obtained (0.14, 0.85, and 2.1  $\mu$ g/L) may thus be considered minimum values. Consequently, the odor threshold of  $\beta$ -damascenone in red wine is probably above 2.1  $\mu$ g/L and certainly above 0.85  $\mu$ g/L. Therefore, the odor threshold of  $\beta$ -damascenone in red wine is probably somewhere between 2 and 7  $\mu$ g/L.

Moreover, from an aromatic point of view, the odor thresholds obtained apparently correlated with the fruity complexity of the matrix used. On a scale of increasing aromatic complexity, the very neutral model white wine was followed by model red wine 2, with very little fruity character, and then model red wine 1, with its strong caramel and candied fruit aromas. The odor thresholds determined showed exactly the same increasing scale. So, even in matrices without any trace of  $\beta$ -damascenone, the odor threshold increases with the complexity of the matrix.

**Table 1** presents the free  $\beta$ -damascenone and the  $\beta$ -damascenone precursor concentrations obtained in whole wines analyzed by GC-MS. Results show contents globally close to 1  $\mu$ g/L for both free  $\beta$ -damascenone and  $\beta$ -damascenone precursors (on average 998  $\pm$  460 and 812  $\pm$  491  $\mu$ g/L, respectively). Values for Bordeaux wines (the first nine wines on the table) were in the range obtained by Kotseridis et al. (20, 22). Considering the perception threshold range for  $\beta$ -damascenone and levels assayed in wines, none of the wines tested had sufficiently high concentrations for the compound to be perceptible in their aroma. Furthermore, the distinctive apple aroma of  $\beta$ -damascenone was not recognized or identified in these red wines.

**Table 3.** Volatile and Range of Concentrations in ng/L Tested to Determine a Possible Indirect Aromatic Impact of  $\beta$ -Damascenone

	test 1	test 2	test 3	test 4	test 5	test 6	test 7	test 8
session 1: ethyl cinnamate		model base wine				model base wine + 50 ng/L $\beta$ -damascenone		
	300	700	1000	1500	300	700	1000	1500
session 2: ethyl caproate		model base wine + $\beta$ -damascenone 50 ng/L				model base wine		
	10	20	30	40	10	20	30	40
session 3: IBMP		model base wine + 50 ng/L $\beta$ -damascenone				model base wine		
	2	4	6	8	2	4	6	8

**Table 4.**  $\beta$ -Damascenone Odor Thresholds in ng/L

water/ethanol solution	model white wine	model red wine 1	model red wine 2	red wine
50	140	2100	850	7000

Concentrations of  $\beta$ -damascenone precursors in wines make it possible to evaluate the quantity of potentially hydrolyzable compounds, able to increase the concentration of free volatile. That point is, nevertheless, debatable as, until now, no precise data on changes in  $\beta$ -damascenone concentrations in red wines are available. Like all glycoconjugated precursors,  $\beta$ -damascenone precursors may be acid hydrolyzed during wine aging and storage, thus increasing the free  $\beta$ -damascenone concentration (9, 10, 13). However,  $\beta$ -damascenone may also be oxidized into odorless hydroxy- $\beta$ -damascone (13), thus reducing the free  $\beta$ -damascenone concentration. Moreover,  $\beta$ -damascenone may react with free sulfur dioxide to give odorless carbonyl bisulfite. Free sulfur dioxide level may so influence  $\beta$ -damascenone contribution to wine aroma. The total free  $\beta$ -damascenone and  $\beta$ -damascenone precursors only give an approximation of the maximum potential  $\beta$ -damascenone concentration, if all of the  $\beta$ -damascenone precursors were hydrolyzed without any further degradation of these compounds and without combination to sulfur dioxide. Even taking the total amount into account, concentrations were generally closer to 2  $\mu$ g/L (1810  $\pm$  789 ng/L, on average), that is, lower than or, in the best case, equal to the  $\beta$ -damascenone odor threshold in red wine. These data may appear to contradict the latest results on the impact of  $\beta$ -damascenone on wine aroma. The most recent publications (5, 7, 26, 27) highlighted  $\beta$ -damascenone's high OAV and suggested that this compound had a direct contribution to the varietal aromas of red wines. According to Guadagni et al. (28), who first defined it, the OAV of an aromatic volatile corresponds to the ratio of this aromatic volatile's concentration in a given matrix to the aromatic volatile's odor threshold in the same matrix. However, the "wine" matrix was not taken into account in previous OAV calculations. In fact, the  $\beta$ -damascenone content in wine was divided by the  $\beta$ -damascenone odor threshold in water or hydroalcoholic solution. The "OAV" values obtained in this way were not really OAVs, as defined by Guadagni et al. (28). As demonstrated above, odor thresholds determined in solutions are very different from those in wine, so aromatic impact conclusions for wines based on OAV calculated using  $\beta$ -damascenone odor thresholds in water or model base wine are unlikely to be very accurate. Thus, the potential direct impact suggested in various articles (5, 7, 8, 14, 26, 27) is probably highly overevaluated.

AEDA of wine extract showed that  $\beta$ -damascenone was detected at one of the highest FDs. It was perceived until the third or fourth dilution of the extract, as shown in **Table 5**. Dilutions of pure  $\beta$ -damascenone showed that this volatile was detectable by GC-O at concentrations in the injected solution as low as 5  $\mu$ g/L. Considering the volume injected (2  $\mu$ L), 0.01 ng of  $\beta$ -damascenone was detected in GC-O analyses, a similar

**Table 5.** Average Estimated  $\beta$ -Damascenone Concentrations in Wine Extracts Analyzed by AEDA

	FD <sup>a</sup>	Merlot <sup>b</sup>	Cabernet franc <sup>b</sup>
wine: GC-MS assay		1.042	0.977
wxtract: 90 $\times$ [wine]		<b>93.78</b>	<b>87.93</b>
dilution 1: [extract]/2	<b>2</b>	<b>46.89</b>	<b>43.97</b>
dilution 2: [dilution 1]/2	<b>4</b>	<b>23.45</b>	<b>21.98</b>
dilution 3: [dilution 2]/2	<b>8</b>	<b>11.72</b>	<b>10.99</b>
dilution 4: [dilution 3]/2	<b>16</b>	<b>5.86</b>	5.50
dilution 5: [dilution 4]/2	32	2.93	2.75

<sup>a</sup> Factor of dilution as defined by Grosch (30). <sup>b</sup> Concentrations in  $\mu$ g/L; bold entries are wine extracts or dilutions of wine extracts where  $\beta$ -damascenone was detected.

quantity to the 0.046 ng reported by Ong and Acree (23). Furthermore, a wine extract may contain 90-fold more concentrated  $\beta$ -damascenone than the initial wine sample, depending on sample preparation procedures. Considering the concentration factor, it was totally logical that  $\beta$ -damascenone would be detected in the first three or four dilutions of the extracts, but not in the fifth, as shown in **Table 5**.  $\beta$ -Damascenone was only detected by AEDA in wine extracts or dilutions of wine extracts where the estimated concentration was above the 5  $\mu$ g/L detection threshold. The question whether  $\beta$ -damascenone concentrations detected in wine extract are representative of wine aroma may be explored by comparing the odor and detection thresholds obtained in wine and GC-O, respectively. In fact, the 5  $\mu$ g/L detection threshold obtained by GC-O corresponds to a  $\beta$ -damascenone concentration in wine of approximately 50–60 ng/L, that is considerably lower than the odor thresholds obtained in model red wines and, a fortiori, in red wine. Contrary to findings in previous research, the major impact of  $\beta$ -damascenone indicated by GC-O analyses of wine extract does not, apparently, reflect its true contribution to the aroma of the original wine. Actually, even though AEDA is a very good method for first investigations, it does not allow one to extrapolate the organoleptic impact of an aromatic compound from an analytical detection threshold. Globally, the major impact of  $\beta$ -damascenone in AEDA only reflects its very low detection threshold in GC-O: Even if only imperceptible concentrations are present in red wines, this may be one of the preponderant compounds identified in olfactometric analyses.

Ethyl cinnamate and ethyl caproate are two odorants, characterized in tasting by "strawberry", "red berry", or simply "fruity" descriptors. They are well-known for their contribution to the fruity aroma of red wines, while IBMP, with its green pepper aroma, is noted for its herbaceous overtones. Odor threshold determinations for these three odorants demonstrated an interaction with  $\beta$ -damascenone, as summarized in **Table 6**. Indeed, when  $\beta$ -damascenone was added to model wine solution for triangular tests, the odor thresholds of both ethyl cinnamate and ethyl caproate were lower, confirming results obtained by Ferreira et al. (7) who indicated that, in model media, a significant decrease in fruity and caramel aromas was observed when  $\beta$ -damascenone was absent and concluded that  $\beta$ -dama-

**Table 6.** Odor Thresholds in ng/L for Three Volatiles, with and without  $\beta$ -Damascenone in the Matrix

volatile	hydroalcoholic solution	hydroalcoholic solution + 50 ng/L $\beta$ -damascenone
ethyl cinnamate	above 1500	1450
ethyl caproate	34.5	25
IBMP	5.5	6.5

scenone acted as an aroma enhancer. On the contrary, when the model base wine contained  $\beta$ -damascenone, the judges had greater difficulty in detecting IBMP.

Taken together, the odor threshold determinations carried out during this study may suggest that the impact of  $\beta$ -damascenone on red wines aroma was indirect rather than direct. Although its free, detectable form is present in concentrations too low to be directly perceptible in wines,  $\beta$ -damascenone might act as an enhancer of red fruit aromas in red wine, either directly, by lowering the perception thresholds of some "red fruit" volatiles, or indirectly, by increasing the odor threshold of IBMP. This possible enhancer role of  $\beta$ -damascenone has to be carefully investigated; results come from blends of only two volatile, while in wines, they are several centuries. It could be done according to methods of aroma models and omission tests, proposed by both Guth and Ferreira et al. (7, 29).

In conclusion,  $\beta$ -damascenone is characterized by a very wide range of odor thresholds, depending on the matrix used; it is very low in aqueous alcoholic solutions and in much higher thresholds in wines. Moreover,  $\beta$ -damascenone has a very low detection threshold in GC-O analyses; indeed, it is among the compounds detected at the highest FD in AEDA. These two findings frequently led to the conclusion that  $\beta$ -damascenone had a significant direct impact on red wine aromas. However, a comparison of the  $\beta$ -damascenone odor thresholds in model base wines and red wine with the concentrations found in red wines revealed that it apparently had no direct impact on red wine aroma. It would be more interesting to study  $\beta$ -damascenone's indirect contribution, possibly acting as an enhancer of fruity aromas.

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