

Formation and Degradation of Furfuryl Alcohol, 5-Methylfurfuryl Alcohol, Vanillyl Alcohol, and Their Ethyl Ethers in Barrel-Aged Wines

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Furfural, 5-methylfurfural, and vanillin co-occurred in 64 barrel-aged red, white, and model wines with the reduction products, furfuryl alcohol, 5-methylfurfuryl alcohol, and vanillyl alcohol, and with the corresponding ethyl ethers of these alcohols. Hydrolytic studies in a model wine have shown that 5-methylfurfuryl ethyl ether is formed rapidly from 5-methylfurfuryl alcohol, but both decomposed quickly under the conditions. Vanillyl ethyl ether was also formed relatively rapidly, and both this ether and vanillyl alcohol were stable in the model wine. The formation of furfuryl ethyl ether from furfuryl alcohol and the subsequent decomposition of these two compounds were comparatively slow. The relative concentration of these aromatic alcohols and ethers in the barrel-aged wines was consistent with the observed stability of the furan derivatives, but low concentrations of vanillyl alcohol and vanillyl ethyl ether observed in all samples showed that factors other than solvolytic degradation were responsible for reducing the concentration of these compounds in wine. Furfuryl ethyl ether, which had an aroma threshold of 430 $\mu\text{g/L}$ in a white wine, was found at approximate concentrations of up to 230 $\mu\text{g/L}$ in the wines.

Keywords: Wine; oak; furfural; 5-methylfurfural; vanillin; furfuryl ethyl ether; 5-methylfurfuryl ethyl ether; vanillyl ethyl ether; hydrolysis

INTRODUCTION

Volatile components of oakwood are extracted into wine during barrel maturation and can have a profound influence on wine flavor. Aromatic aldehydes form a major proportion of such volatiles (Boidron et al., 1988; Towey and Waterhouse, 1996), yet the sensory role of these aldehydes is still largely a matter for conjecture. Opinion on the sensory impact of aromatic aldehydes is largely based on threshold data of individual compounds in non-oaked wines and does not take into account the possibility of sensory interactions with other volatiles derived from oak or from microbial activity during the maturation phase. Thus, threshold data (Boidron et al., 1988) suggest that vanillin can have a strong influence on wine aroma, while furfural and 5-methylfurfural have, on their own, no more than a minor impact. However, furfural has been reported to have an important modifying effect on the perception of the aroma of oak lactones in wine (Reazin, 1981). The concentration of oak-derived aromatic aldehydes (and, indirectly, their reduction products) in barrel-aged wines depends, inter alia, on coopering heat (Chatonnet et al., 1989).

Whatever the sensory impact of such aldehydes, it will be diminished by transformations of these compounds to other products during barrel-aging. It is well-known

that microbiological reduction to the corresponding alcohols can account for decreases in furfural, 5-methylfurfural, and vanillin observed during barrel-aging and that these alcohols are formed in wine mostly, if not entirely, by this mechanism (Boidron et al., 1988; Chatonnet et al., 1992a). However, the organoleptic role (and fate) of such reduction products in wine is not well understood.

This paper reports the co-occurrence, in barrel-aged wines, of furfural, 5-methylfurfural, and vanillin, together with furfuryl alcohol, 5-methylfurfuryl alcohol, vanillyl alcohol, and their corresponding ethyl ethers, and discusses the degradation of these compounds during wine storage. The wines are the same as those that were the subject of an earlier study (Spillman et al., 1997).

MATERIALS AND METHODS

Materials. Details of oak selection, vinification, and wine maturation in oak barrels have been given previously (Sefton et al., 1993a; Spillman et al., 1997). Vanillin, vanillyl alcohol, furfural, furfuryl alcohol, and 5-methylfurfural were obtained from commercial sources. *5-Methylfurfuryl alcohol* was prepared by reduction of a solution of 5-methylfurfural (500 mg) in dry dioxane (10 mL) with lithium aluminum hydride (150 mg) at room temperature over 30 min. *Furfuryl ethyl ether* and *5-methylfurfuryl ethyl ether* were prepared by heating a mixture of the corresponding alcohol (200 mg), sodium hydride (100%, 100 mg), and iodoethane (1 mL) to 80 °C under a nitrogen atmosphere overnight. *Vanillyl ethyl ether* was synthesized by allowing a solution of vanillyl alcohol (1 g) and perchloric acid (70%, 1.5 mL) in ethanol (50 mL) to stand at

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room temperature overnight. The reaction was quenched with saturated aqueous sodium bicarbonate (25 mL) and the solvent evaporated in vacuo. All of the above products were isolated with ether and purified by distillation with a Kugelrohr apparatus. [$^2\text{H}_3$]Vanillyl alcohol (*i.e.* 4-hydroxy-3- $^2\text{H}_3$ methoxybenzyl alcohol) was prepared as follows. A solution of sodium borohydride (208 mg) in water (25 mL) was added dropwise at a rate of 1 mL/min to a solution of [$^2\text{H}_3$]vanillin (1.11 g; Spillman et al., 1997) in water (70 mL). This mixture was stirred at 25 °C for 3.5 h. Perchloric acid (0.2 M) was then added dropwise at a rate of 1 mL/min until a pH of 4 was reached. Sodium chloride (60 g) was added, and the solution was extracted with ethyl acetate (6 × 25 mL). The organic extract was washed with a solution of 2 drops of sodium bicarbonate in saturated aqueous sodium chloride (5 × 1 mL) and dried (Na_2SO_4). Removal of the solvent in vacuo yielded [$^2\text{H}_3$]vanillyl alcohol (1.13 g), which was recrystallized from 1,2-dichloroethane as clear rectangular crystals (97% yield). [$^2\text{H}_3$]Vanillyl ethyl ether (*i.e.* 4-hydroxy-3- $^2\text{H}_3$ methoxybenzyl ethyl ether) was prepared from [$^2\text{H}_3$]Vanillyl alcohol in the same manner as the unlabeled material. Mass spectra, m/z (%): furfuryl ethyl ether, 126 (M, 40), 98 (8), 97 (15), 95 (5), 82 (35), 81 (100), 70 (8), 69 (15), 53 (35), 51 (10), 42 (15), 41 (15), 39 (15); 5-methylfurfuryl ethyl ether, 140 (M, 40), 112 (3), 111 (10), 109 (5), 96 (20), 95 (100), 83 (5), 81 (5), 69 (5), 67 (5), 65 (5), 55 (4), 53 (5), 52 (5), 51 (5), 43 (12); vanillyl ethyl ether, 182 (M, 52), 181 (7), 153 (6), 151 (5), 138 (30), 137 (100), 125 (8), 123 (15), 122 (18), 107 (8), 106 (9), 94 (12), 93 (18), 65 (12); [$^2\text{H}_3$]vanillyl alcohol, 157 (M, 100), 140 (35), 128 (30), 93 (51), 65 (40); [$^2\text{H}_3$]vanillyl ethyl ether, 185 (M, 53), 184 (7), 156 (5), 141 (23), 140 (100), 123 (10), 122 (13), 93 (15).

Analysis. All compounds analyzed in the wines were identified by comparison of GC retention time and mass spectra with those of authentic samples. Extracts of wines were prepared and analyzed for furfural, furfuryl alcohol, furfuryl ethyl ether, 5-methylfurfural, 5-methylfurfuryl alcohol, and 5-methylfurfuryl ethyl ether, using 2,5-dimethylphenol and 4-methyl-2,6-bis(1,1-dimethylethyl)phenol as internal standards, as described previously (Sefton et al., 1993a). The concentration of furfural, furfuryl alcohol, 5-methylfurfural, and 5-methylfurfuryl alcohol in the extracts was determined from the peak areas of total ions or of specific fragment ions monitored in the samples, in dichloromethane solutions of reference standards, and in extracts of wines to which spiked standard additions of reference compounds had been made. The concentration of furfuryl ethyl ether and 5-methylfurfuryl ethyl ether in the extracts was estimated by assuming a 1:1 response with the internal standards when analyzed by GC/MS. Specific ion fragments monitored were m/z 95 and 96 for furfural, m/z 81 and 98 for furfuryl alcohol, m/z 81 and 126 for furfuryl ethyl ether, m/z 109 and 110 for 5-methylfurfural, m/z 95 and 112 for 5-methylfurfuryl alcohol, and m/z 95 and 140 for 5-methylfurfuryl ethyl ether. Red wines that had been cellar stored in bottles for 2 years following the oak maturation phase [see Spillman et al. (1997)] were analyzed for furfuryl alcohol according to the method of Marsal and Sarre (1987).

Extracts of wines were prepared for analysis for vanillyl alcohol and vanillyl ethyl ether as follows. For vanillyl alcohol determinations, [$^2\text{H}_3$]vanillyl alcohol (200 ng) in water (20 μL) was added to the wine (1 mL). The wine sample was passed through a preconditioned (methanol, then water washed) phenyl solid phase extraction cartridge (500 mg; Alltech, catalog no. 232300). The cartridges were then eluted with dichloromethane (3 mL) without prior washing with water and the eluents concentrated to ~1 mL prior to analysis by GC/MS. Attempts to prepare samples for vanillyl alcohol analysis by loading larger volumes of wine or by washing the cartridges following adsorption gave lower recoveries of analyte and standard. No analyte or standard was recovered when C_{18} cartridges were used or when wines were extracted directly with organic solvents. For vanillyl ethyl ether analysis, ether extracts of wines to which [$^2\text{H}_3$]vanillyl ethyl ether (100 $\mu\text{g/L}$) had been added were prepared as described for the analysis of vanillin (Spillman et al., 1997). Calibration curves for

vanillyl alcohol and vanillyl ethyl ether were obtained by spiked standard additions to white wine. Vanillyl alcohol was added to give concentrations of 10, 20, 50, 100, 250, 500, 1000, and 2000 $\mu\text{g/L}$ in the wine. Vanillyl ethyl ether was added to give concentrations of 5, 10, 50, 100, and 150 $\mu\text{g/L}$. The calibration curves obtained were linear. The correlation coefficient for vanillyl alcohol was 1.000, and the correlation coefficient for vanillyl ethyl ether was 0.999.

For the determination of vanillyl alcohol and vanillyl ethyl ether in all wines, and of furfuryl alcohol in bottle-stored wines, a Hewlett-Packard benchtop gas chromatograph/mass spectrometer (GC/MS) was used. The Hewlett-Packard 5890A series II gas chromatograph was fitted with a 30 m × 0.25 mm J&W fused silica capillary column DB-1701, 0.25 μm film thickness. The oven temperature was started at 60 °C, held at this temperature for 2 min, then increased to 250 °C at 10 °C/min, and held at this temperature for 20 min. The injector was held at 220 °C and the transfer line at 275 °C. The sample volume injected was 3 μL . The splitter, at 30:1, was opened after 36 s. Positive ion electron impact spectra at 70 eV were recorded in the range m/z 35–450 for scan runs. For quantification of vanillyl alcohol and vanillyl ethyl ether, mass spectra were recorded in the selective ion monitoring (SIM) mode. The ions monitored in SIM runs were m/z 140 and 185 for [$^2\text{H}_3$]vanillyl ethyl ether (internal standard); m/z 137, and 182 for vanillyl ethyl ether, m/z 128, 140, and 157 for [$^2\text{H}_3$]vanillyl alcohol (internal standard), and m/z 125, 137, and 154 for vanillyl alcohol. Selected fragment ions were monitored for 50 ms.

Hydrolysis of Furfurylic and Benzylic Alcohols in Model Wine. A solution of furfuryl alcohol (10.46 mg), 5-methylfurfuryl alcohol (2.44 mg), vanillyl alcohol (1.92 mg), benzyl alcohol (1.83 mg), and 4-methyl-2,6-bis(1,1-dimethylethyl)phenol (1.12 mg) in model wine (10% aqueous ethanol, pH adjusted to 3.4 with tartaric acid and potassium hydrogen tartrate, 100 mL) was divided into 9 mL aliquots. These were sealed under a nitrogen atmosphere in 10 mL ampules, and the ampules were heated at 45 °C in a constant-temperature oven. Ampules were cooled and opened at intervals of 4 h, 8 h, 16 h, 1 week, 4 weeks, and 16 weeks. The contents were extracted with diethyl ether (2 mL, followed by 6 × 1 mL), the ether extracts were combined and concentrated to ~1 mL under a stream of nitrogen, and the concentrated extract was analyzed with the Hewlett-Packard benchtop GC/MS. The ratio of the peaks for benzyl alcohol and 4-methyl-2,6-bis(1,1-dimethylethyl)phenol in the chromatograms of the various extracts did not vary significantly, and no products that could be ascribed as being derived from these compounds were observed. This indicated that no significant reaction of either compound took place. Accordingly, changes in concentration of furfuryl alcohol, 5-methylfurfuryl alcohol, vanillyl alcohol, and the ethyl ethers of these compounds were estimated by a comparison of peak heights for these compounds with those for benzyl alcohol and 4-methyl-2,6-bis(1,1-dimethylethyl)phenol.

Aroma Threshold of Furfuryl Ethyl Ether. The aroma threshold of furfuryl ethyl ether in a neutral dry white wine was determined according to American Society for Testing and Materials (ASTM) method E 679-79, using 26 judges. The wine had a free sulfur dioxide content of ~50 mg/L. Wines were presented in ascending order of furfuryl ethyl ether concentration, at 5.5, 16.7, 50, 150, 450, 1350, 4050, and 12150 $\mu\text{g/L}$.

RESULTS AND DISCUSSION

Concentration of Furfural, 5-Methylfurfural, Vanillin, and Their Corresponding Alcohols in Red, White, and Model Wines. Furfural and Furfuryl Alcohol (Table 1). Reduction of furfural to furfuryl alcohol was apparent in all of the barrel-aged wines and even in the stainless steel stored red wine control. Biological mechanisms for furfural reduction in wine are well-known (Boidron et al., 1988; Chatonnet et al.,

Table 1. Mean Concentration (Milligrams per Liter) of Furfural and Furfuryl Alcohol in Barrel-Aged Red, White, and Model Wines

wine (barrels)	11 weeks of aging		55 weeks of aging		93 weeks of aging	
	furfural	furfuryl alcohol	furfural	furfuryl alcohol	furfural	furfuryl alcohol
red (24)					0.10	6.3 (98%) ^a
red control ^b					{0.05} ^e	{3.1 (1%)}
white (24) ^c			2.2	3.6 (65%)	{N/A} ^f	{N/A}
white (9) ^{c,d}	1.4	9.6 (87%)	{2.1}	{1.5 (20%)}		
model (16) ^c	{0.5}	{2.3 (6%)}	2.4	3.5 (64%)		
			{2.1}	{1.1 (20%)}		
			6.1	0.37 (7%)	9.7	1.5 (17%)
			{2.8}	{0.61 (14%)}	{5.5}	{1.8 (19%)}

^a Numbers in parentheses are the mean value of [furfuryl alcohol] × 100/[furfuryl alcohol + furfural] for each barrel. ^b Stored in stainless steel. ^c Neither furfural nor furfuryl alcohol was detected in the white or model wine controls. ^d Subset of the 24 barrels. ^e {} standard deviations for the mean concentration data and for the mean percentages. ^f N/A not applicable.

1992a), although the possibility of chemical reduction also taking place in wines cannot be excluded.

The red wines, which were analyzed after 93 weeks aging, contained very little furfural. In each barrel, 97% or more of the total pool of furfural plus furfuryl alcohol, consisted of the reduced form, which was found in amounts ranging from 2 to 15 mg/L. This indicates that extensive reduction of furfural had occurred in all barrels during the maturation period, even though alcoholic and malolactic fermentations were complete prior to the commencement of oak maturation. The growth of microflora in red wines during oak barrel maturation has been demonstrated by several authors (Chatonnet et al., 1992b, Millet et al., 1995). The relative proportion of furfural and furfuryl alcohol in the barrels is entirely consistent with the data reported by Chatonnet et al. (1990, 1992a).

The white wine alcoholic fermentations were completed in 24 barrels. After a period of 11 weeks, the wine in each barrel was racked off its yeast lees and the barrels were rinsed. Each wine was then transferred back to the barrel from which it was taken and aged for a further 44 weeks. The wines were not inoculated for malolactic fermentation, but this process nevertheless occurred spontaneously in some of the barrels during weeks 11–55 of the maturation period. The concentration of furfural and furfuryl alcohol was determined in the wines in the 24 barrels at the end of the 55 week period and also in a subgroup of 9 of these barrels immediately following racking (Table 1).

Reduction of furfural in the white wines had apparently taken place to a lesser extent in the white wines than in the red. After 55 weeks in wood, the proportion of the total pool of furfural plus furfuryl alcohol that existed in the reduced form varied considerably, from 28 to 99%, and this proportion was positively correlated with the consumption of malic acid in the wines ($p < 0.001$; Sefton et al., 1993b). Thus, the amount of furfuryl alcohol may have been determined mainly by the extent of the malolactic fermentation. In those barrels (14) in which <10% of the malic acid had been consumed, the proportion of furfuryl alcohol varied between 28 and 72%, whereas in the five barrels containing less than half of the initial amount of malic acid, this proportion was more than 93%.

Reduction of furfural was, as expected, least apparent in the model wines (Table 1). The free SO₂ concentration in the model wines in the barrels was periodically adjusted to 30 mg/L, and the wines were screened on seven occasions during the 93 week storage period for

the presence of yeast and bacteria. The contents of the barrels were sterilized by the addition of 0.15 mL of dimethyldicarbonate/L of model wine when yeast or bacteria colony forming units (cfu) were detected at >0.2 cfu/mL. One barrel at one sampling showed 36 yeast cfu/mL, but all others showed <7 (usually 0) yeast or bacteria cfu/mL. Nevertheless, furfuryl alcohol appeared in all barrel-stored model wines, indicating that there was microbiological activity in these barrels for at least part of the storage period. The proportion of furfuryl alcohol in the total pool of furfural plus furfuryl alcohol was ≤10% in 10 of the 16 barrels, but in 4, around half of the furfural originally extracted appears to have been reduced.

5-Methylfurfural and 5-Methylfurfuryl Alcohol. The mean concentrations of 5-methylfurfural and 5-methylfurfuryl alcohol in the wines are shown in Table 2. In contrast to furfural, 5-methylfurfural makes up most of the total pool of 5-methylfurfural plus 5-methylfurfuryl alcohol. This is not, however, because 5-methylfurfural is resistant to transformations in wine, as there was considerably less of this compound in the red and white wines than there was in the model wines. Rather, it is clear that the concentration of the corresponding alcohol does not account for the apparent loss of 5-methylfurfural.

Vanillin and Vanillyl Alcohol. The accumulation of vanillin in the wines from these barrels has been discussed previously (Spillman et al., 1997). The lower concentrations of vanillin in the red and white wines compared to those in the model wines were attributed to microbiological transformations of vanillin in the former. In the white wines, this apparently occurred only during barrel fermentation and maturation on lees, i.e. during the first 11 weeks of barrel storage. In contrast to the effect on furfural, malolactic fermentation in the white wines had no significant effect on vanillin concentration.

Vanillyl alcohol was found in low concentration only in the red, white, and model wines at the end of their respective maturation periods. The mean concentrations for these wine types were 22, 9, and 12 μg/L, respectively. A higher concentration was determined in the white wines sampled at racking (after 11 weeks), ranging from 42 to 61 μg/L with a mean of 50 μg/L. As was the case with 5-methylfurfural, the amount of vanillyl alcohol observed here does not account for the apparent loss of vanillin (200–400 μg/L) during barrel maturation of the red and white, compared with the model, wines (Spillman et al., 1997).

Table 2. Mean Concentration (Milligrams per Liter) of 5-Methylfurfural (5-MF) and 5-Methylfurfuryl Alcohol (5-MFA) in Barrel-Aged Red, White, and Model Wines

wine (barrels)	11 weeks of aging		55 weeks of aging		93 weeks of aging	
	5-MF	5-MFA	5-MF	5-MFA	5-MF	5-MFA
red (24)					0.07	0.01 (20%) ^a
red control ^b					{0.06} ^e	{0.003 (13%)}
					nd ^f	0.005
					{N/A} ^g	{N/A}
white (24)			0.24	0.027 (14%)		
			{0.16}	{0.005 (8%)}		
white (9) ^c	0.37	0.024 (6%)	0.27	0.026 (13%)		
	{0.08}	{0.006 (1%)}	{0.018}	{0.003 (9%)}		
white control ^b	nd	0.006	nd	0.017		
	{N/A}	{N/A}	{N/A}	{N/A}		
model (16) ^d			0.90	0.003 (0.4%)	1.16	0.006 (0.8%)
			{0.35}	{0.001 (0.3%)}	{0.51}	{0.002 (1.1%)}

^a Numbers in parentheses are the mean value of [5-methylfurfuryl alcohol] × 100/[5-methylfurfuryl alcohol + 5-methylfurfural] for each barrel. ^b Stored in stainless steel. ^c Subset of the 24 barrels. ^d Neither 5-methylfurfural nor 5-methylfurfuryl alcohol was detected in the model wine controls. ^e {} standard deviations for the mean concentration data and for the mean percentages. ^f nd, not detected. ^g N/A not applicable.

Table 3. Mean Concentration (Milligrams per Liter) of Vanillyl Ethyl Ether (VEE), Furfuryl Ethyl Ether (FEE),^a and 5-Methylfurfuryl Ethyl Ether (5-MFEE)^a in Barrel-Aged Red, White, and Model Wines

wine (barrels)	11 weeks of aging		55 weeks of aging		93 weeks of aging		VEE	FEE	5-MFEE
	VEE	FEE	5-MFEE	VEE	FEE	5-MFEE			
red (24)							0.004	0.080	nd ^b
red control ^c							{0.005} ^f	{0.037}	{N/A} ^g
							nd	0.002	nd
							{N/A}	{N/A}	{N/A}
white (24)				0.011	0.098	0.011			
				{0.005}	{0.032}	{0.015}			
white (9) ^d	0.010	0.042	0.034	0.010	0.094	0.015			
	{0.002}	{0.010}	{0.010}	{0.003}	{0.035}	{0.014}			
white control ^c	0.001	nd	nd	0.003	0.002	nd			
	{N/A}	{N/A}	{N/A}	{N/A}	{N/A}	{N/A}			
model (16) ^e				0.004	0.009	nd	0.006	0.024	0.004
				{0.001}	{0.017}	{N/A}	{0.002}	{0.034}	{0.007}

^a FEE and 5-MFEE are approximate concentrations only (see text). ^b nd, not detected (<0.001 mg/L). ^c Stored in stainless steel. ^d Subset of the 24 barrels. ^e None of the ethers were detected in the model wine control. ^f {} standard deviations for the mean concentration data. ^g N/A, not applicable.

Identification of the Ethyl Ethers of Furfuryl, 5-Methylfurfuryl, and Vanillyl Alcohol in the Wines. The conversion of vanillin to vanillyl alcohol and further transformation products during fermentation in beer or wine has been noted by several authors (Chatonnet et al., 1992a and references cited therein). In a previous study of the constituents generated during fermentation (Humphries et al., 1992), we similarly observed the conversion of added vanillin to vanillyl alcohol during fermentation in a model medium. A second (unknown) product of vanillin transformation was also observed but not reported. This product (M⁺ 182) accounted for ≈10–12% of the vanillin originally added to the ferment (on the assumption that equimolar responses for vanillin and its transformation products on GC/MS). The mass spectrum and retention time on gas chromatography suggested that it was the ethyl ether of vanillyl alcohol, and this has now been confirmed by comparison with a synthetic sample.

Subsequent analyses have shown that vanillyl ethyl ether is present in barrel-aged wines and is also a trace component of model wine extracts of oakwood shavings, presumably as a product of ethanolysis of lignin. The formation of vanillyl ethyl ether in wine can be attributed to the reactivity of the activated benzylic carbon in vanillyl alcohol. To our knowledge, vanillyl ethyl ether has not been previously reported as a wine component. It has been previously observed as a constituent of vanilla extracts (Galetto et al., 1978).

Following confirmation of vanillyl ethyl ether as a wine constituent, the presence of the corresponding furfuryl ethers in wines was also sought. The two compounds were identified in chromatograms of extracts of the wines from interpretation of the spectra, and assignments were confirmed by comparison with synthetic samples. Furfuryl ethyl ether had been previously reported as a wine constituent (Bertuccioli and Viani, 1976) and, more recently, as a staling compound in beer (Harayama et al., 1995), but to our knowledge 5-methylfurfuryl ethyl ether has not been previously reported as a wine constituent.

Vanillyl ethyl ether was quantified in the barrel-aged wine samples by stable isotope dilution analysis. It was found in all wines in low concentration only, ranging in concentration from 2 (in some red wines) to 20 μg/L in a 55-week-aged white wine. Mean data are shown in Table 3.

Only semiquantitative data for furfuryl- and 5-methylfurfuryl ethyl ether were obtained (Table 3), as the chromatograms of the extracts of the wines had been obtained prior to the identification of these compounds. 5-Methylfurfuryl ethyl ether was found in highest concentration in the white wines. After 11 weeks (corresponding to racking), the concentration ranged from ≈20 to 50 μg/L in the nine barrels examined, while after 55 weeks, this compound was not detected at all in some barrels, although in others it was found at up

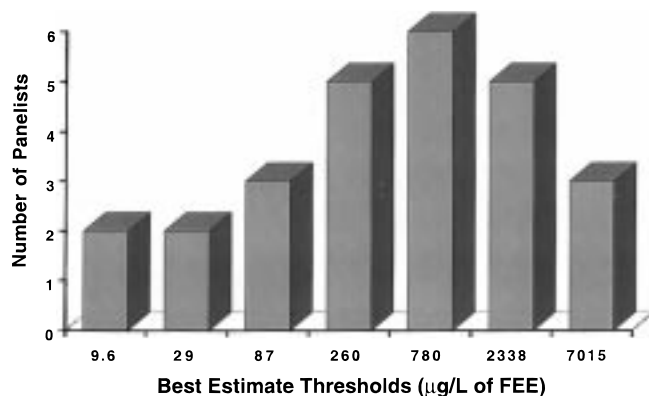


Figure 1. Best-estimate aroma thresholds of furfuryl ethyl ether (FEE) in a neutral dry non-oaked white wine.

to 60 µg/L. 5-Methylfurfuryl ethyl ether was virtually absent from the red wines (<2 µg/L in all barrels).

Furfuryl ethyl ether also varied considerably in concentration among the wines. It ranged in approximate concentration from 25 to 60 µg/L in the white wines after 11 weeks of aging, from 40 to 170 µg/L in the white wines after 55 weeks of aging, and from 30 to 230 µg/L in the red wines.

Informal assessment indicated that concentrated solutions (1 mg/mL) of vanillyl- and 5-methylfurfuryl ethyl ether in model wine had little or no odor, and so aroma thresholds were not determined. These compounds presumably make no contribution to wine flavor. On the other hand, the synthetic sample of furfuryl ethyl ether had a strong solvent/kerosene-like aroma at this concentration. It has a reported detection (by taste) threshold in beer of 2.5 µg/L and was seen as adding an astringent note in this medium at 6 µg/L (Harayama et al., 1995). These authors also found that addition of a combination of furfuryl ethyl ether and (*E*)-2-nonenal to beer reproduced the stale character typical of aged samples. The latter compound has recently been identified as an oak component which can be found in red wines (Chatonnet and Dubourdieu, 1997).

The aroma threshold of furfuryl ethyl ether in a neutral non-oaked white wine was determined using a panel of 26 members. The distribution of individual best-estimate thresholds is shown in Figure 1. The group best-estimate threshold was 430 µg/L. This compound might therefore make a contribution to the aroma and flavor of at least some wines, but such a contribution will depend on its sensory interaction with other oak components.

Reactivity of the Benzylic Alcohols and Their Ethyl Ethers. At the completion of the maturation of the red and white wines, vanillyl alcohol and vanillyl ethyl ether were present at low levels only (<10%) in terms of the vanillin, which had apparently been transformed during the maturation period. This contrasts with the relatively high proportion of vanillyl alcohol (up to 75% of the initial vanillin concentration) reported as present immediately following fermentation in model media in the presence of added vanillin (Chatonnet et al., 1992a; Humphries et al., 1992). In this study, there was considerably more vanillyl alcohol in the white wines at 11 weeks (mean concentration of 50 µg/L) than at 55 weeks (mean concentration of 9 µg/L). Most of the vanillyl alcohol, together with its ethyl ether, appears to have been further degraded during the maturation period. The concentration of 5-methylfur-

Table 4. Mass Spectra of Products Formed from Hydrolysis of Furfuryl Alcohol and 5-Methylfurfuryl Alcohol^a

product	mass spectrum, <i>m/z</i> (%)
A	112 (20), 97 (70), 69 (25), 59 (10), 55 (8), 54 (7), 53 (7), 43 (100)
B	112 (35), 97 (40), 69 (25), 55 (4), 54 (4), 53 (3), 43 (100)
C	126 (50), 98 (100), 97 (40), 82 (20), 81 (50), 70 (65), 69 (35), 56 (18), 55 (35), 54 (15), 53 (80), 52 (15), 51(15), 44 (18), 43 (40), 42 (45), 41 (30)
D	115 (25), 87 (5), 73 (5), 45 (8), 43 (100)
E	144 (5), 129 (25), 102 (15), 101 (18), 99 (60), 74 (18), 73 (15), 71 (12), 57 (8), 56 (8), 55 (10), 45 (10), 43 (100)
F	87 (35), 43 (100)
G	115 (25), 87 (5), 73 (5), 45 (5), 43 (100)
H	206 (70), 177 (3), 161 (100), 147 (25), 133 (7), 131 (6), 125 (10), 115 (10), 109 (7), 105 (8), 103 (7), 97 (40), 95 (15), 91 (18), (60), 79 (10), 77 (8), 69 (7), 65 (10), 53 (15), 52 (10), 51 (9)

^a Entries are listed in increasing order of GC retention time

furyl alcohol plus 5-methylfurfuryl ethyl ether was similarly low in most barrels.

The ease of formation of the benzylic ethyl ethers from the corresponding alcohols, as well as the stability of these compounds in model wines, was examined by heating a solution containing furfuryl, 5-methylfurfuryl, vanillyl, and benzyl alcohols in model wine (pH 3.4) at 45 °C for 16 weeks.

5-Methylfurfuryl ethyl ether was observed after 4 h of heating and reached a maximum concentration (≈20% of the starting alcohol) after 8 h. Thereafter, the concentration of both the ether and alcohol decreased, with no trace of either compound remaining after 1 week at 45 °C. Vanillyl ethyl ether was also formed rapidly and was also observed after 4 h of heating. In contrast to the 5-methylfurfuryl derivatives, however, both vanillyl alcohol and vanillyl ethyl ether appeared to be stable under the reaction conditions. Approximately 80% of the vanillyl alcohol was converted to the ether after 1 week, and the concentration of these compounds was essentially unchanged during the next 16 weeks of heating.

Furfuryl alcohol reacted considerably more slowly than either the 5-methyl analogue or vanillyl alcohol. Approximately 5% was converted to the ether after 1 week, and the concentration of the latter compound reached a plateau at 15% conversion after 4 weeks. The concentration of furfuryl alcohol decreased continuously, however, and after 16 weeks, only one-third of the original furfuryl alcohol could be accounted for in terms of either the alcohol or ether.

Benzyl alcohol was apparently stable under the reaction conditions, and neither the ethyl ether nor any other transformation products were seen during the course of the reaction.

Along with the three ethers, eight other compounds were formed during the course of the reaction. The mass spectra of these products are given in Table 4. Compound **E** had a mass spectrum identical to that of ethyl 4-oxopentanoate, while compound **H** may be 5-(furfuryl)furfuryl ethyl ether (interpretation of mass spectrum). The other six products remain to be identified. Compounds **A**, **B**, **D**, **F**, and **G** were formed relatively rapidly and appear to be products of 5-methylfurfuryl alcohol, while compounds **C**, **E**, and **H** are presumed to be products of furfuryl alcohol.

The observed transformations of the four alcohols are governed by their reactivity at the benzylic position and

the apparent susceptibility of the furan (but not benzene) ring to acid-catalysed ring opening in simple protic solvents. The order of reactivity of the alcohols to ether formation, which is governed by the relative stability of the corresponding benzylic cations, was 5-methylfurfuryl > vanillyl >> furfuryl >>> benzyl. For the furan alcohols/ethers, the 5-methyl substituent would be expected to enhance the rate of protonation of the furan ring and subsequent formation of solvolysis products.

The data recorded in Tables 1–3, and also by others (Chatonnet et al., 1990, 1992a), are consistent with the observed reactivity of furfuryl and 5-methylfurfuryl alcohol. The sum of the concentration of 5-methylfurfural plus the corresponding alcohol and ethyl ether is substantially less in the red and white wines than in the model wines, and this disparity is greatest in the red wines, which biological reduction is apparently more complete, and the wines have been in wood long enough for most, if not all, of the 5-methylfurfuryl alcohol and the corresponding ether to have decomposed. The highest concentration of 5-methylfurfuryl ether was measured in the white wines at racking (i.e. after 11 weeks). Shorter periods are optimal for the ether to accumulate without extensive decomposition.

Furfuryl ethyl ether was found in higher concentration in the red wines, and the white wines at 55 weeks, reflecting the slower rate of formation and decomposition of this compound, compared to that of 5-methylfurfuryl ethyl ether. Decomposition, although slow, can nevertheless account for the disparity between the sum of the concentration of furfural plus furfuryl alcohol and furfuryl ethyl ether in the red and white wines compared to that in the model wines. This disparity was not as great as with the 5-methyl analogues, which decomposed more rapidly.

Chemical decomposition of furfuryl alcohol in the red wines continued during 2 years after bottling, following the 93 week barrel maturation period. The percentage decrease in furfuryl alcohol concentration among the 24 bottled samples ranged from 68% to 82%, with a mean decrease of 73%.

Furfuryl ethyl ether can be formed in beer from furfuryl acetate, a presumed fermentation product (Harayama et al., 1995). These authors concluded that the ether was formed via furfuryl alcohol which was in turn derived from hydrolysis of the acetate. The data reported in their paper, however, are equally consistent with the formation of furfuryl ethyl ether directly from the acetate, via solvation of the furfuryl carbocation. We have not, as yet, found furfuryl acetate in wines, although wines that have been barrel fermented and which are at an early stage of maturation may prove to be a source of this compound.

The observed low concentration of vanillyl alcohol and vanillyl ethyl ether in the wines is due to factors other than simple solvolytic degradation. The biological transformations suggested by Chatonnet et al. (1992a) could account for a diminution of vanillyl alcohol (and hence also vanillyl ethyl ether, which exists in equilibrium with the alcohol) during storage; however, given the ease of formation of the benzylic cation from vanillyl alcohol, as evidenced by the facile formation of the ethyl ether, condensation reactions with, for example, nucleophilic sites on grape polyphenols could equally account for the low concentration seen in the wines.

Similar alkylations by furfuryl and 5-methylfurfuryl cations could contribute to the loss of furfurylic alcohols

and ethers during wine aging, and the possibility of microbiological transformations of these compounds should also not be excluded.

CONCLUSION

Aromatic aldehydes are readily reduced biologically in wines, and furfural appears to be particularly susceptible to this transformation, being reduced during both alcoholic and malolactic fermentation and even by low levels of microflora in model wines that were repeatedly treated to minimize such biological activity. Once formed, the reduction products can be converted to the corresponding ethers, and both ethers and alcohols are then further transformed. In the case of the furfuryl and 5-methylfurfuryl (but not vanillyl) derivatives, this is in part, if not in whole, by simple solvolytic mechanisms. Biochemical transformations and chemical reactions with other wine components may also account for losses of these compounds in wine.

Other than the tentatively identified and short-lived 5-methylfurfurylthiopropionate (Chatonnet et al., 1991), the known products of biological and chemical transformations of vanillin and 5-methylfurfural during wine-making and maturation are of no apparent sensory consequence. On the other hand, furfuryl alcohol and furfuryl ethyl ether are more stable in wines and may, in combination with other oak components, contribute to wine flavor. Whatever the sensory impact of these compounds, it will diminish with bottle-aging.

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