

A Powerful Aromatic Volatile Thiol, 2-Furanmethanethiol, Exhibiting Roast Coffee Aroma in Wines Made from Several *Vitis vinifera* Grape Varieties

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The chemical compound 2-furanmethanethiol (2FM), with a strong roast coffee aroma, has been identified in sweet white wines made from the Petit manseng grape variety, and in certain red Bordeaux wines (made from the Merlot, Cabernet franc, and Cabernet sauvignon grape varieties). This was done by extracting specific volatile thiols using *p*-hydroxymercuribenzoate. The 2FM has also been found in toasted oak used in barrel-making. All the Petit manseng sweet white wines and some of the red Bordeaux wines analyzed contained between a few ng/L and several dozen ng/L of 2FM. Taking into account its very low perception threshold (0.4 ng/L in a model hydro alcoholic environment), 2FM could therefore contribute to the roast coffee aroma of certain wines.

Keywords: 2-Furanmethanethiol; Petit manseng; red Bordeaux wines; *Vitis vinifera*; barrel; Maillard reaction

INTRODUCTION

Volatile thiols are very strong-smelling molecules that can affect the aroma of numerous foods such as fruit, grilled meat, etc. (Shankaranarayana, 1982). Several compounds in this family, contributing to the typical aroma of certain varietal wines, have recently been identified. 4-Mercapto-4-methylpentan-2-one, having a strong box tree odor, was first isolated in Sauvignon blanc (Darriet et al., 1995), and subsequently in Scheurebe wines (Guth, 1997). 3-Mercaptohexyl acetate and 3-mercaptohexan-1-ol, observed in passion fruit (Engel and Tressl, 1991), has also been found in Sauvignon blanc (Tominaga et al., 1996, 1998a) and Cabernet sauvignon wines (Bouchilloux et al., 1998a). The assay of volatile thiols in Sauvignon blanc has confirmed the presence of 4-mercapto-4-methylpentan-2-one, 3-mercaptohexyl acetate, and 3-mercaptohexan-1-ol, which have characteristic odors reminiscent of box tree, grapefruit, and passion fruit, respectively (Tominaga et al., 1998b). Similarly, the role of 2-mercaptoethyl acetate and 3-mercaptopropyl acetate, having toasty and roast meat odors, has been clearly demonstrated in certain dry white wines (Sémillon and Sauvignon blanc) (Lavigne et al., 1998). 2-Methyl-3-furanthiol, with an empyreumatic odor, has also been identified in wine (Bouchilloux et al., 1998b).

This article identifies and assays for 2FM, which has a well-known roast coffee aroma (Reichstein and Staudinger, 1926) in wines made from several grape varieties.

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MATERIALS AND METHODS

Wines Analyzed. Sweet white wines made from Petit manseng (Domaine Cauhapé: Symphonie de novembre and Noblesse du temps; 1997, 1996, and 1995 vintages) from an estate in the Jurançon appellation (France). These wines were made from late-harvest grapes picked in successive waves, which then achieved overripeness through "raisining".

The red Bordeaux wines that were analyzed came from the Graves (Château Carbonnieux from the 1996, 1995, and 1994 vintages) and Pomerol appellations (Château Trotanoy from the 1996, 1995, 1994, and 1989 vintages). All the wines analyzed were barrel-aged.

Specific Extraction of Volatile Thiols. (a) From the Wine. The volatile thiols were specifically extracted from the wine using the method described by Tominaga et al. (1998b), but modified as follows. Wine was extracted by dichloromethane, without adjusting the pH to 7. The *p*-hydroxymercuribenzoate (*p*-HMB), used to extract thiols during the organic phase, was prepared in a Tris solution (0.2 M) (without adjusting the pH). The rinsing swab for the Dowex column (0.1 M sodium acetate) was prepared without NaCl. **(b) From Toasted Oak.** Three oak barrel staves were toasted in the same way as is generally done at the Seguin Moreau cooperage (Merpins, France). The parameters of the three toasting levels tested (light, medium, and heavy) have been described by Chatonnet and Boidron (1989). A thickness of 1–2 mm was then scraped off each stave. The shavings, corresponding to the three toasting levels (20 g), as well as a control sample of nontoasted oak, were placed in dichloromethane (400 mL) for 18 h. The filtered organic phase was extracted by a *p*-HMB (20 mL × 2) solution.

Calibration. The 2FM reference solutions (Aldrich, F2,040-8) were prepared in a wine (white or red) lacking this compound (10–80 ng/L). For each concentration, the wine's volatile thiols were extracted using the method described above.

GC/MS, GC/FPD, and GC/Olfactometry. The chromatographic conditions of GC/MS were identical to those described by Tominaga et al. (1998b), but a BPX-5 column (SGE, 50 m × 0.22 mm, 0.25 μm) was used for identification. For analyses on the BP-20 column, detection was achieved in SIM mode by selecting the ion (*m/z* = 114). The GC/FPD and

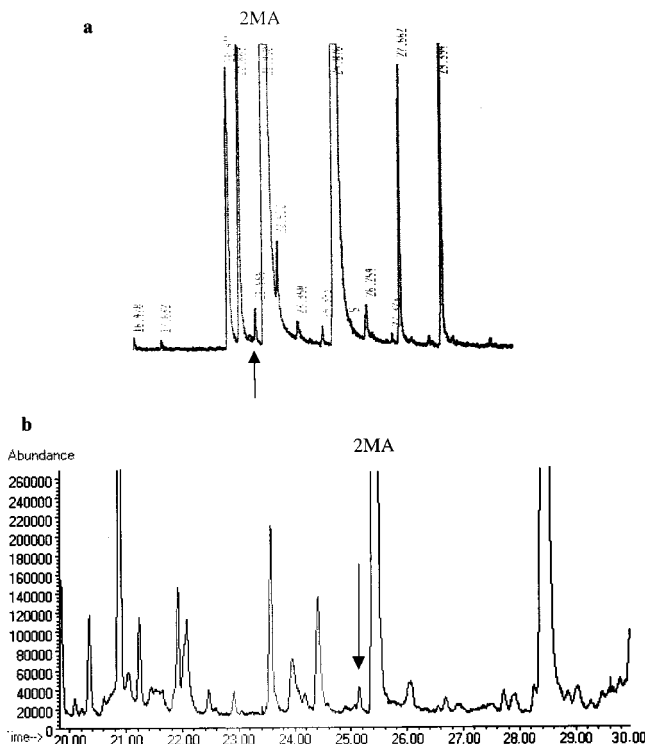


Figure 1. Analysis by GC/FPD (a) and GC/MS (b) of volatile thiols extracted from a red Bordeaux wine (Château Carbonnieux 1994). 2MA: 2-mercaptoethyl acetate.

GC/Olfactometry analysis conditions were identical to those described by Chatonnet et al. (1992) and by Darriet et al. (1991), respectively.

Repeatability. Five successive analyses (extraction and assay) were carried out for each wine lacking 2FM spiked with 15 ng/L of this compound, to establish a coefficient of variation.

Olfactory Perception Threshold. This was measured according to the method described by Boidron et al. (1988), using a triangular test with a jury.

RESULTS AND DISCUSSION

Specific Extraction of Volatile Thiols A method for the specific extraction of volatile thiols in white wines (Tominaga et al., 1998b), using *p*-HMB, has already been described. For the purposes of this study, the method was modified to a certain extent so that it could also be applied to red wines.

To avoid the formation of quinones, at a basic pH, which could react with thiols, the dichloromethane extraction of volatile compounds in wine was done without altering the pH of the wine to 7. This modification also required changing the composition of the *p*-HMB solution used to extract volatile thiols from the organic phase. During this stage, it is imperative that the *p*-HMB does not precipitate in the aqueous phase by acidification of the latter. This was managed by preparing a Tris solution (0.2 M) which kept the pH above 7 during the formation of complex *p*-HMB-thiols. When the extraction method is modified in this way, the selective extraction method of volatile thiols by *p*-HMB can be used with all types of wine.

Identifying 2FM in Wine Using GC/MS. Extracts of volatile thiols obtained from 1.5 L of white wine (1996; Jurançon) and red wine (1994; Château Carbonnieux) were analyzed by GC/Olfactometry, GC/FPD, and GC/MS. The GC/FPD chromatogram using the BPX-5 column showed a peak (see arrow in Figure 1a) corre-

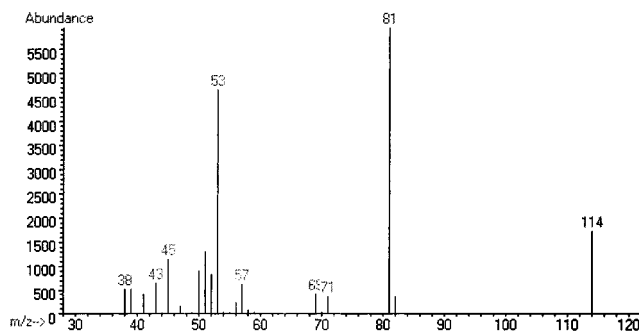


Figure 2. Mass spectrum of a peak marked with an arrow in Figure 1b.

Table 1. Repeatability of the Assay of 2FM of a Wine Added to 15 ng/L of This Compound

samples	2FM (ng/L)
1	16.5
2	15.0
3	14.1
4	14.8
5	15.0
av ($n = 5$)	15.1
SD	0.8
CV (%) (5%)	4.1

sponding to a strong aromatic zone just before the 2-mercaptoethyl acetate (2MA) (Lavigne et al., 1998) having a flavor of grilled meat. This was reminiscent of roasted coffee (Figure 1a).

This compound was identified by GC/MS with electron impact. The peak (Figure 1b) corresponding to the retention time for the roast coffee smelling compound presented a mass spectrum with fragments characteristic of 2FM (Figure 2). The retention time of this peak was the same as for a reference compound.

Standard Curve and Repeatability. The standard curve for the 2FM assay was prepared on a BP-20 column. It was not separated from the 2-mercaptoethyl acetate, which can exist in sizable quantities in some white and young red wines. The assay was able to be carried out on this column by detecting the selected 114 ion, absent from the mass spectrum of the 2-mercaptoethyl acetate.

In the concentration range (10–80 ng/L), the control curve was linear: $[2FM] \text{ (ng/L)} = 275.7H/His - 0.819$, $r = 0.998$ (H : height of 2FM peak; His : height of internal standard peak). This standard curve was measured using the height of the peaks rather than peak areas, because the chromatogram showed a small contaminated peak just after the 2FM.

The repeatability of the assay was confirmed by a series of five extractions. Table 1 shows the coefficient of variation. It was lower than 5%.

Perception Threshold of 2FM in a Model Solution. 2FM is a particularly strong-smelling compound reminiscent of roasted coffee. Its perception threshold in a model hydro alcoholic solution is extremely low (0.4 ng/L). According to Tressl and Silwar (1981) and Tressl et al. (1980), it has a strong roast coffee aroma at levels between 0.01 and 0.5 $\mu\text{g/L}$.

2FM Content in Wines. The 6 Petit manseng wines analyzed all contained 2FM (Table 2). The levels found varied according to when the grapes were harvested. For certain vintages (such as 1997 and 1996, which were the ripest), wines made from grapes picked during the third wave of picking contained 1.5 to 2 times as

Table 2. Assay (ng/L) of 2FM in Various Petit Manseng Wines, According to the Vintage and When the Grapes Were Picked

vintages	samples	
	symphonie de novembre (first wave)	noblesse du temps (second+third wave)
1997	41	62
1996	31	52
1995	37	36

Table 3. Assay (ng/L) of 2FM in Various Red Bordeaux Wines

samples			samples		
Châteaux	vintages	2FM	Châteaux	vintages	2FM
Ch. Carbonnieux	1996	17.1	Ch. Trotanoy	1996	4.4
	1995	18.1		1995	11.3
	1994	25.0		1994	11.1
	1993	22.6		1989	2.0

Table 4. Assay of 2FM in Sauvignon Blanc and Petit Manseng Wines Aged in New and Used Oak Barrels

varieties	used oak barrel (ng/L)	new oak barrel (ng/L)
Sauvignon blanc	0.42	0.44
Petit manseng (first wave)	39	36

many thiols as those picked during the first wave. The concentration was as high as 60 ng/L, which is considerable compared to the perception threshold.

The presence of 2FM in the red wines analyzed was not consistent (Table 3). The highest concentration (25 ng/L) never reached that found in most of the Petit manseng wines. The concentration/perception threshold ratio of 2FM in some of the red wines was nevertheless high. It is therefore very likely that this compound contributed to their roast coffee aromas.

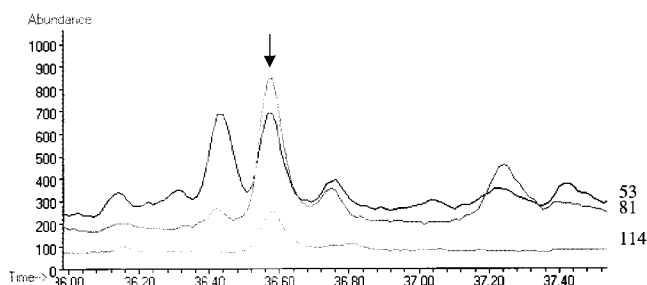
Identifying 2FM in Toasted Oak. 2FM was absent from the staves before toasting. However, all the toasted staves contained quantifiable amounts (Figure 3) of 2FM (approximately 0.2 ng/g of shavings).

It is well-known that 2FM can be caused by a Maillard reaction, as with roasted coffee and broth from roasted meat (Drumm and Spanier, 1991; Farmer et al., 1989). Although it has never previously been identified, it is not surprising to find this compound in oak that has been heated to about 165 °C for 5–10 min.

The presence of 2FM in staves does not exclude the possibility that this compound may also be formed in wine for other mechanisms. For instance, Sauvignon blanc wines do not contain any 2FM, whether they are fermented in new or used oak barrels (Table 4); the same experiment done with Petit manseng showed that levels of this compound were the same when fermented in new barrels or used ones. Furthermore, all the red wines aged in new oak barrels did not contain the same quantity of 2FM. Thus, 2FM could not come directly from toasted staves.

CONCLUSION

2FM, a volatile thiol, has been identified for the first time in sweet white wines made from the Petit manseng grape variety, and in certain red Bordeaux wines. In light of its characteristic odor and its extremely low perception threshold, this volatile thiol may contribute to the "roast coffee" and "toasty" aroma in certain wines. 2FM was also found in the toasted oak staves of barrels used to age wine.

**Figure 3.** Chromatogram of the extract of toasted oak obtained with three selected ions ($m/z = 53$, $m/z = 81$, $m/z = 114$). The retention time of the peak indicated by an arrow corresponds to 2FM.

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