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## INTRODUCTION

Sulphur compounds, especially volatile thiols, make a positive contribution to the varietal aroma of certain fruits and wines. Since the 1990s, several highly odoriferous thiols have been identified in wines. The first molecule identified as a characteristic component of Sauvignon blanc wine aroma was 4-mercapto-4-methyl-pentan-2-one (4MMP) (1). This compound has a characteristic aroma described as black currant, boxwood and broom. In certain Sauvignon blanc wines, the 4MMP revealed concentrations as high as 40 ng/l, considerably higher than the perception threshold (0.8 ng/l in model solution, 3 ng/l in white and red wines), confirming its decisive organoleptic role in wines (2). Other volatile thiols were later identified in Sauvignon blanc wines: 3-mercaptohexyl acetate (3MHA), 4-methyl-4-mercaptopentan-2-ol and 3-mercaptohexan-1-ol (3MH), smelling of boxwood and zest, citrus zest, and grape fruit and passion fruit, respectively. These compounds were also identified as a key odorant of Gewürztraminer, Riesling, Petit Manseng, Semillon, Sauternes and Cabernet Sauvignon wines (3-5). The 3MH presents an odour detection threshold of 60 ng/l in aqueous ethanol (2).

## AIMS

The aim of this study was to evaluate the presence of these volatile thiols in wines produced from Portuguese white grape cultivars (Antão Vaz, Arinto, Fernão Pires, Verdelho da Madeira and Viosinho). Besides sensory analysis, the wines were analyzed using gas chromatography coupled to different detectors, namely flame photometric detector (FPD), flame ionization detector (FID), mass-spectrometry (MS) and by olfactometry (O).

## MATERIALS AND METHODS

### Grape musts

Experiments were carried out with white musts obtained from grapes of the *Vitis vinifera* varieties of Sauvignon blanc, Antão Vaz, Arinto, Fernão Pires, Verdelho da Madeira and Viosinho. All wines were produced in 2009. The Arinto and Fernão Pires wines were also produced in 2010.

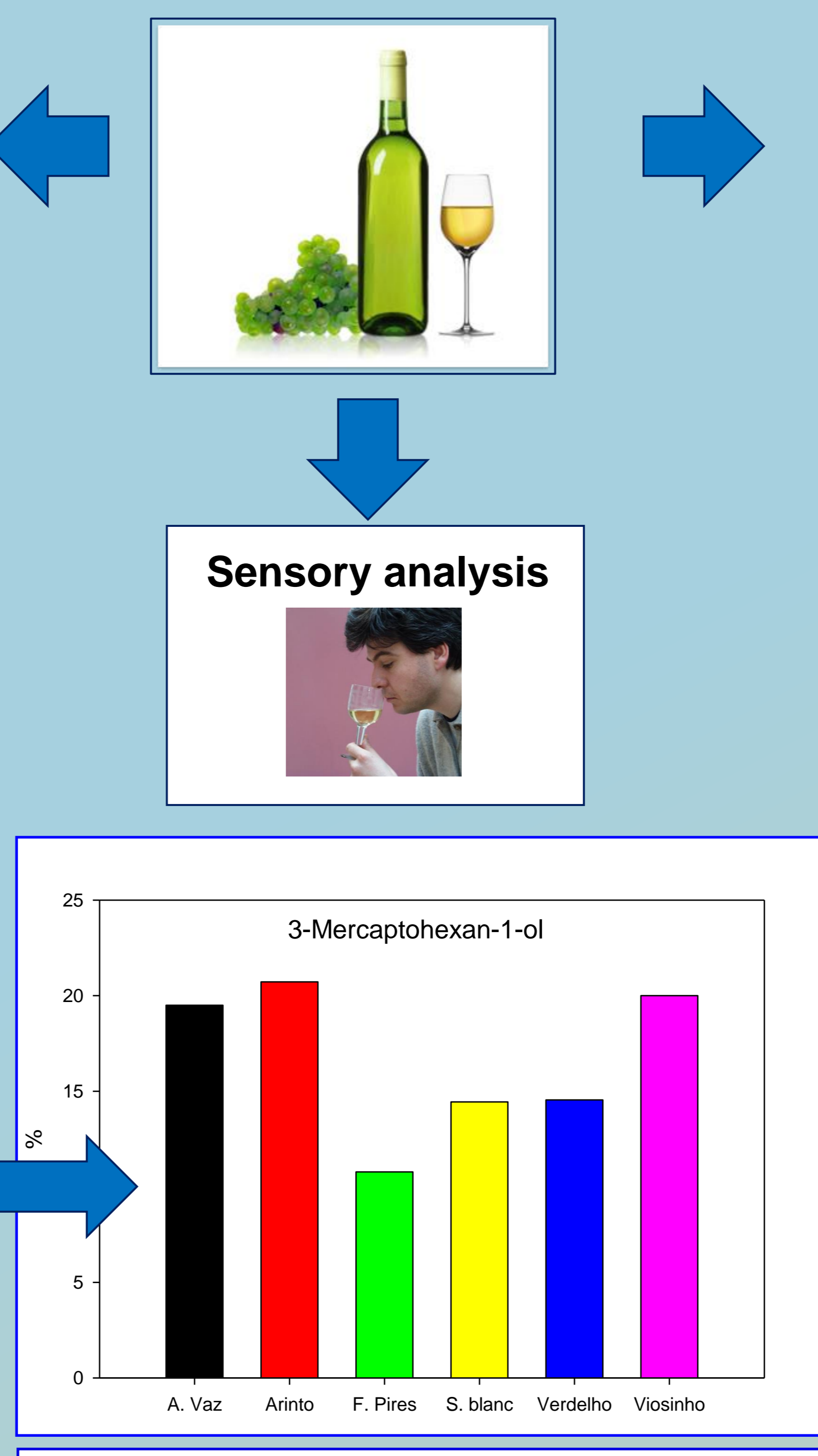
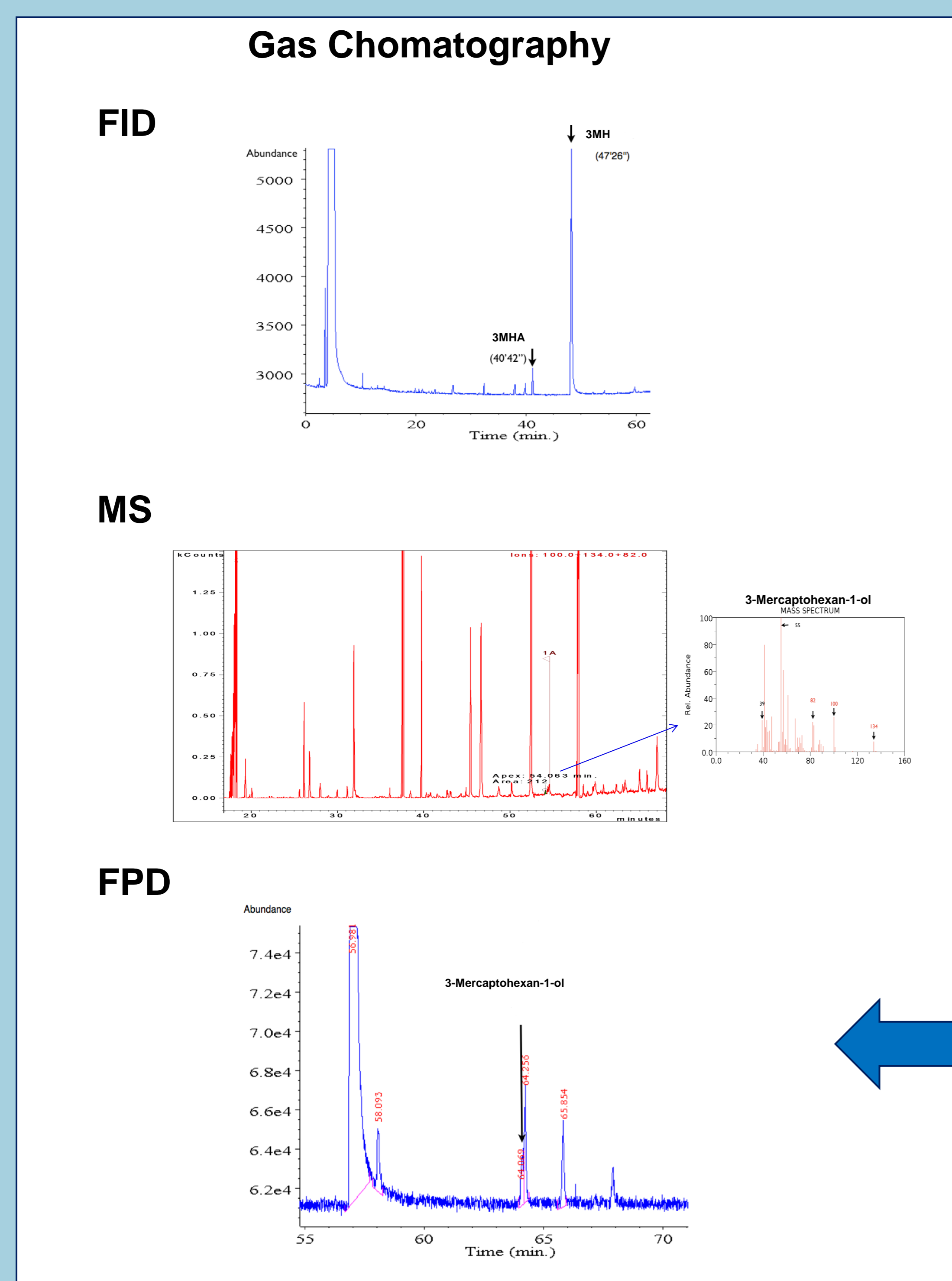
### Analytical determinations

Sulphur compounds were determined by gas chromatography with flame photometric detection (GC/FPD), according to the method described by Moreira *et al.* (7). The methods reported by Oliveira e Silva *et al.* (8) were used to perform GC-mass spectrometry (GC-MS) and GC-O analysis. A Hewlett-Packard 5890 gas chromatograph, equipped with a flame ionization detector was also used, according to the method described by Moreira *et al.* (9).

### Sensory analysis

Wines were tested randomly regarding their aromatic composition. The panel was composed by 10 experienced wine tasters.

## RESULTS



### GC-olfactometry

Table 1. Kovats retention index, descriptor/olfactory zone, chemical compound, and aroma intensity of different wines.

KRI (I)	KRI (II)	Descriptor/Olfactory zone	Chemical compound	Antão Vaz	Arinto	Fernão Pires	Sauvignon blanc	Verdelho da Madeira	Viosinho	Arinto (2010)	Fernão Pires (2010)
1398	1394 <sup>a</sup>	Black currant/box	4MMP	1	1	1	3	2	1	1	2
1741	1735 <sup>a</sup>	Box/passion fruit	3MHA	0	0	0	0	0	0	2	1
1883	1872 <sup>a</sup>	Sweaty/passion fruit	3MH	3	3	2	2	2	3	3	3

KRI (I): Kovats retention index calculated; KRI (II): Kovats retention index obtained from literature. <sup>a</sup>Ferreira *et al.* (9); <sup>b</sup>Cullere *et al.* (10).  
4MMP: 4-mercapto-4-methyl-pentan-2-one; 3MHA: 3-mercaptohexyl acetate; 3MH: 3-mercaptohexan-1-ol.  
0: not detected; 1: low intensity; 2: medium intensity; 3: high intensity.

## CONCLUSIONS

This work highlights the presence of volatile thiols (4MMP, 3MH, 3MHA) in wines from Antão Vaz, Arinto, Fernão Pires, Verdelho da Madeira and Viosinho varieties.

The GC-FPD methodology used in this work allows obtaining some interesting results on the 3MH level in wines. Further work is needed to quantify volatile thiols in other Portuguese white wines.

## BIBLIOGRAPHY

- (1) Darriet, P., Tominaga, T., Lavigne, V., Boidron, J.N., Dubourdiou, D. 1995. Identification of a powerful aromatic component of *Vitis vinifera* L. var. Sauvignon wines: 4-mercapto-4-methyl-pentan-2-one. *Flavour and Fragrance Journal*, 10: 385-392.
- (2) Capone, D., Sefton, M., Hayasaka, Y., Jeffery, D. 2010. Analysis of precursors to wine odorant 3-mercaptohexan-1-ol using HPLC-MS/MS: resolution and quantification of diastereomers of 2-S-cysteinylhexan-1-ol and 3-S-glutathionylhexan-1-ol. *Journal of Agricultural and Food Chemistry*, 58: 1390-1395.
- (3) Tominaga, T., Ballesterwick-Guyot, R., Gaschons, C.P., Dubourdiou, D. 2000. Contribution of volatile thiols to the aromas of white wines made from several *Vitis vinifera* grape varieties. *American Journal of Enology and Viticulture*, 51: 178-181.
- (4) Tominaga, T., Furrer, A., Henry, R., Dubourdiou, D., 1998. Identification of new volatile thiols in the aroma of *Vitis vinifera* L. var. Sauvignon blanc wines. *Flavour and Fragrance Journal*, 13: 159-162.
- (5) Roland, A., Schneider, R., Le Guernevé, C., Razungles, A., Cavelier, F. 2010. Identification and quantification by LC-MS of a new precursor of 3-mercaptohexan-1-ol (3MH) using stable isotope dilution assay: elements for understanding the 3MH production in wine. *Food Chemistry*, 121: 847-855.
- (6) Moreira, N., Mendes, F., Guedes de Pinho, P., Vasconcelos, I. 2004. Analysis of sulphur compounds using gas chromatography with flame photometric detection. *Analytica Chimica Acta*, 513: 183-189.
- (7) Oliveira e Silva, H., Guedes de Pinho, P., Machado, B., Hogg, T., Marques, J.C., Câmara, J., Albuquerque, F., Silva Ferreira, A. 2009. Impact of forced-aging process on Madeira wine flavor. *Journal of Agricultural and Food Chemistry*, 56: 11989-11996.
- (8) Moreira, N., Pina, C., Mendes, F., Couto, J.A., Hogg, T., Vasconcelos, I. 2011. Volatile compounds contribution of *Hanseniaspora guilliermondii* and *Hanseniaspora uvarum* during red wine vinifications. *Food Control*, 22: 662-667.
- (9) Ferreira, V., Aznar, M., Lopez, R., Cacho, J. 2001. Quantitative gas chromatography olfactometry carried out at different dilutions of an extract. Key differences in the odor profiles of four high-quality Spanish aged red wines. *Journal of Agriculture & Food Chemistry*, 49: 4818-4824.
- (10) Cullere, L., Escudero, A., Cacho, J., Ferreira, V. 2004. Gas chromatography olfactometry and chemical quantitative study of the aroma of six premium quality Spanish aged red wines. *Journal of Agricultural and Food Chemistry*, 52: 1653-1660.

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