Eur Food Res Technol (2002) 214:441–443
DOI 10.1007/s00217-001-0467-9

ORIGINAL PAPER

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Application of a new analytical method to determine the susceptibility of wine to browning

Received: 6 September 2001 / Revised: 14 November 2001 / Published online: 16 March 2002

Abstract Differences in the phenolic composition of 12 commercial Fino sherry wines were determined by HPLC. These wines showed different susceptibilities to browning. Measuring their absorbances at 420 nm, their natural evolutions after bottling were monitored. The results were compared to the results obtained by the application of a new accelerated browning method based upon the electrochemical oxidation of wines. A good agreement between the natural evolution and the accelerated method results was obtained.

Keywords Phenolic compounds · Browning · Wine

Introduction

Browning is the most serious phenomenon of degradation suffered by white wines after bottling. It results in serious economic losses for wine-producing companies. Therefore, the determination of the susceptibility of white wines to the phenomenon of browning is of considerable industrial interest.

Previously, it has been proven that the susceptibility of wine to browning is not proportional to phenolic composition [1]. Hence, it is difficult to determine the susceptibility of wine to browning on the basis of its phenolic composition [2]. Among phenolic compounds, flavan-3-ols are the compounds most directly related to the browning process in most of the white wines [3]. Cinnamates are also involved in the browning reactions [4], and in some wines, browning depends on the cinnamates more than on the flavan-3-ols. Cavas from Spain [5] and Fino sherry wines [6] are two of this type of wine. The biological aging of Fino sherry wines can be related to this special behaviour, because high amounts of acetaldehyde are produced by the aging yeast, even over 300 mg/l. Acetaldehyde can promote the polymerization of the flavan-3-ols and therefore the browning reactions are different in these wines [7].

The accelerated methods used to determine the susceptibility of wines to browning are based on heating the wine to different temperatures for different periods of time, together with submitting them to aeration or to oxygenation [8, 9]. The lack of reliability of predictions made by this method has been demonstrated, as well as the lack of similarity between wines browned in this way and those browned naturally [10].

Given this, an analytical technique for determining the susceptibility of wine to browning by means of electrochemical oxidation of the polyphenolic components in the wine has been devised [11].

In this paper, the reliability of the predictions based on this new technique for a number of different types of bottled white wines has been studied. The same samples have also been allowed to evolve naturally. Once the phenomenon had developed, the results of the natural evolution were compared with the results from applying the new analytical technique.

Three types of wines were used in this study: Fino from Jerez (FJ), Fino from Montilla (FM) and Manzanilla from Sanlúcar (MS). All of them are dry white wines from Andalucía, Spain. The aging system used is the same for all three wines e.g. the Solera and Criaderas system, typical of Jerez.

FJ and MS wines are made from the same variety of grape (cv. Palomino Fino). However, MS is aged in Sanlúcar de Barrameda, whereas FJ is aged in El Puerto de Santa María or in Jerez. The differences in phenolic composition are therefore due to very slight differences in climate and to oenological treatment at the end of the wines' aging process.

FM is made in Montilla, Córdoba. The most important difference between FM and the other wines is the grape used to make it (cv. Pedro Ximénez). The winemaking process and the aging system are very similar to FJ and MS wines.

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Materials and methods

Materials. The samples submitted to this trial consisted of nine dry (Fino) sherry wines (named FJ1 to FJ9), one Manzanilla wine (named MS) (Jérez-Xérès-Sherry y Manzanilla de Sanlúcar de Barrameda, Cádiz, Spain) and two Fino type wines of Montilla (named FM1 and FM2) (Montilla-Moriles, Córdoba, Spain). Each wine corresponded to a different commercial brand. All the samples were obtained commercially on the same date. A total of four bottles of each were analysed, and the accelerated browning method was applied in duplicate on every sample. The absorbance at 420 nm was measured after 3 months of natural evolution.

Analysis of the polyphenolic composition. A volume of 100 ml of wine was extracted using 80 ml of diethyl ether by means of continuous rotary extraction, following the method of Brú et al. [12]. 2, 5-Dihydroxybenzaldehyde was used as internal standard.

HPLC analysis. The chromatographic analysis was performed by HPLC in a Waters chromatographic system: M-45 and 510 pumps, model 717 automatic injector, UV-440 detector, Millennium 2.0 software (Waters, Milford, Mass.), using a LiChrospher column (Merck, Darmstadt, Germany). UV detection at 280 nm was used. A gradient elution was used according to the method reported by Guillén et al. [13]. Briefly, two solvents were used: A (10% methanol-2% acetic acid in water) and B (90% methanol-2% acetic acid in water). The initial conditions were a flow rate of 1 ml/min and 100% A, reaching 85:15 (A:B) in 15 min and 50:50 (A:B) in 35 min; both changes were done using a convex gradient. Peak heights were measured automatically and corrected by reference to the internal standard (peak heights were used instead of peak areas because we have found that for these samples they produce better results, as there are several poorly resolved peaks).

Accelerated browning tests. The accelerated browning tests were conducted according to the method previously devised [11] employing a difference of potential of 1.5 V. The sample volume was 125 ml. During the course of the test, the absorbance of the sample was measured at 420 nm. Water was used as reference. The electrochemical oxidation was applied until constant absorbance was obtained.

Natural evolution. Absorbance at 420 nm was measured for monitoring the natural evolution. Measurements were made over 3 months while the bottle remained uncorked but protected by a cotton wool plug to prevent the introduction of foreign substances.

Results and discussion

The phenolic composition of the three types of wine can be observed in Fig. 1; an FJ type wine, an MS type wine and an FM type wine are shown. As can be seen, the three types of wine contain a similar quantity of phenolic compounds. However there are differences in some compounds.

Regarding the most oxidizable compounds, the main differences among these wines are the levels of caftaric acid, gallic acid and caffeic acid (Fig. 1).

Their chemical structures are shown in Fig. 2. They are not the only compounds involved in the browning process. However, in this case, they are some of the compounds involved in browning [14, 15], which are found at different levels of concentration in these wines (Table 1).

Based on the amounts of the most oxidizable compounds, the most susceptible wine to browning should be MS because it contains high concentrations of caftaric and gallic acids. The most resistant wine to browning should be FM because it contains low concentrations of

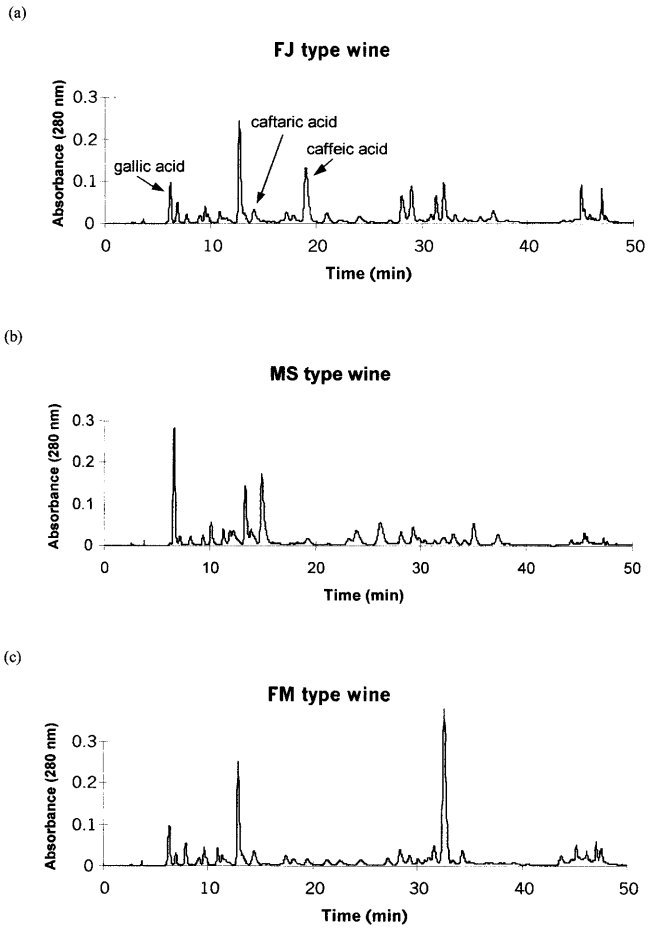

Fig. 1a–c HPLC chromatograms of **a** Fino from Jerez wine, **b** Manzanilla from Sanlúcar and **c** Fino from Montilla

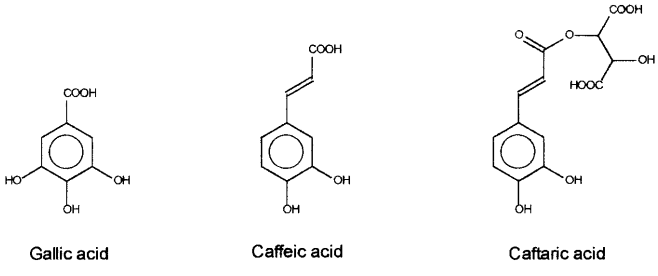

Fig. 2 Structures of gallic acid, caffeic acid and caftaric acid

Table 1 Average amounts of phenolic acids for nine Fino wines from Jerez, one Manzanilla wine and two Fino wines from Montilla

	Fino from Jerez	Manzanilla	Fino from Montilla
Gallic acid mg/l	3.2	10.5	3.7
Caftaric acid mg/l	20.2	23.4	16.1
Caffeic acid mg/l	1.3	0.5	0.3
Catechin mg/l	0.8	0.8	0.7

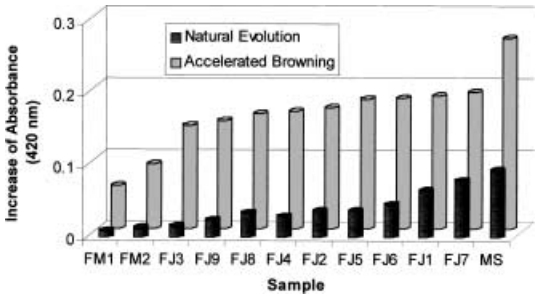

Fig. 3 Natural browning vs. accelerated browning method. *FJ1–FJ9* Jerez type wines, *FM1* and *FM2* Montilla type wines, *MS* Manzanilla type wine

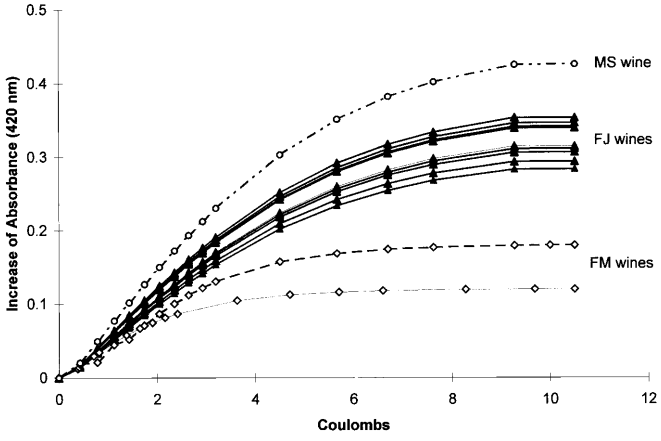

Fig. 4 Absorbance evolution during accelerated browning method development. *FJ* Jerez type wines, *FM* Montilla type wines, *MS* Manzanilla type wine

caftaric, gallic and caffeic acids. At an intermediate level would be FJ wines. Their susceptibility to browning depends on how much of these acids they contain.

In Fig. 3 the change of the absorbance at 420 nm after the natural evolution of the samples over the 3 month period is shown. As can be seen, the wines from Montilla suffered a lower degree of browning than those of Jerez and Sanlúcar. Only one brand of dry sherry from Jerez (FJ3) showed browning as low as that in the wine from Montilla.

The accelerated browning method was applied to the samples at the beginning of the experiment, before starting the natural evolution.

The browning phenomenon develops naturally over a period longer than 3 months, but this time interval is sufficient for an evaluation of the predictions of the method devised. Figure 4 shows the results of the electrochemical oxidation of the wines analysed.

Comparison between the natural results and the predictions of the analytical technique is the best form of validation of such a method as this. Therefore, the values of the natural browning have been compared with the results of the accelerated browning.

By using this analytical technique, it can be seen that there are different susceptibilities to browning. FM wines and one brand of FJ wine presented low susceptibilities, while MS wines presented the highest susceptibility. There were small differences among some FJ wines.

If we compare the increase in absorbance after the application of the accelerated browning with the increase obtained naturally, it is observed that the first is much higher (Fig. 3). This is logical since the wine after 3 months has not reached the condition of maximum browning naturally, in contrast with the accelerated samples, which have reached this condition.

With regard to the predictions of the method devised, it can be checked that they are correct in all cases except for wine FJ4; this wine presented a difference in the order of susceptibility expected from the predictions of the method.

The rest of the samples follow strictly the predictions made by the method. The accelerated method even detected the small differences between the samples from the same zone as in the case of samples FM1 and FM2, both from Montilla. Thus, the capability to predict the browning has been proven.

The method offers considerable advantages over those currently used. The cost of each analysis is extremely low, since effectively only the depreciation of the equipment necessary has to be taken into account, and this equipment is already available in the laboratory of any wine-making company. The time necessary to conduct the test is less than 1 h. For these reasons, this analytical technique could be applied by wine-producing companies to monitor the susceptibility of their wines to the problem of browning.

Acknowledgements The Spanish CICYT (ALI94-0649) supported this work.

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