

Analytical Methods

Extraction of phenolics in liquid model matrices containing oak chips: Kinetics, liquid chromatography–mass spectroscopy characterisation and association with *in vitro* antiradical activity

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Abstract

Four different liquid model matrices were utilised to study the leaching of polyphenols from oak chips. The matrices included distilled water, 12% (v/v) ethanol, 12% (v/v) ethanol adjusted to pH 3.4, and 55% (v/v) ethanol. Extraction of phenolics into the liquid systems was monitored by the estimation of the total polyphenol concentration, using the Folin–Ciocalteu method. The *in vitro* antiradical activity was also recorded using the stable DPPH[•] radical, to ascertain enrichment of the solutions with potentially antioxidant compounds. As a final step, the polyphenolic composition of each matrix was characterised by means of liquid chromatography–electrospray ionisation mass spectrometry. The kinetics of polyphenol leaching into the liquid phase was found to obey a 2nd parameter power equation of the type $y = ax^b$, which produced a good fit of the data ($p < 0.0001$). Kinetics was faster in distilled water up to a point, where after polyphenol extraction occurred at higher rate in the 55% ethanolic solution. The antiradical activity in all cases was highly correlated with total polyphenol concentration ($p < 0.001$), providing that the amount of polyphenols extracted into the liquid media exerted a proportional antioxidant effect. The analytical examination by liquid chromatography–mass spectrometry revealed that the compounds implicated are hydrolysable tannins and hydrolysis products thereof.

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1. Introduction

The ageing process of wines and spirits has an appreciable beneficial influence on their aromatic profile and mouth-feel. Furthermore, a cascade of various transformations of the native grape pigments (anthocyanins), which take place during ageing may provide a higher and long lasting stability of colour (Del Alamo Sanza & Domínguez, 2006; Vivas & Glories, 1996). In recent years there has been an increasing number of studies reporting on the use of wooden chips, which can be incorporated into the ageing

beverage and bring about desirable organoleptic characteristics. Irrespective of the technology implemented to evolve beverage quality, wine or distillate maturation, which takes place in the presence of oak chips, includes processes similar to those encountered in the classic ageing in oak casks. Hydrolysis of wood structural biopolymers (lignins and cellulose) and leaching of hydrolysable tannins and their hydrolysis products (gallic and ellagic acids) can provoke significant alterations in the polyphenolic composition of ageing beverages (Mosedale & Puech, 1998).

The compounds that can be extracted in wines and spirits are primarily ellagitannins, with vescalagin and castalagin being the most representative structures. Hydrolysis products thereof (vescalin, castalin) and dimers (grandinin,

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roburins A–E) can also accompany the predominant forms (Marinov, Dimitrova, & Puech, 1997; Moutounet, Rabier, Puech, Verette, & Barillère, 1989). In addition, usual thermal treatments (toasting) of wooden constituents destined for winemaking purposes or post-extraction transformations may also be crucial in changing the nature of compounds that eventually occur in aged beverages (Puech, Feuillat, & Mosadale, 1999). As a consequence the parameters that can affect extraction of phenolics into ageing beverages merit a deeper investigation.

Fundamental factors that govern polyphenol extraction from oak barrels have been studied to some extent on the basis of model systems (Kadim & Mannheim, 1999), but almost exclusively the outcome has been considered from a technological point of view, whereas the nutritional aspects have been given less attention or even disregarded. Besides the profound effect on the sensory profile of wines and spirits, the enrichment in potentially bioactive wood constituents becomes an issue of high importance. Ellagitannins from various sources, and also ellagic acid have been shown to possess a variety of bioactivities and pharmacological potency (Clifford & Scalbert, 2000), and for this reason the examination of their presence in food commodities should embrace a wider approach.

In this study, simple model matrices composed of hydro-alcoholic mixtures were utilised, to investigate their effect on the leaching rate of polyphenols from oak chips. This allowed the comparison on the basis of the kinetics established. Moreover, the *in vitro* antiradical activity was monitored, in an effort to ascertain if the amount of polyphenols extracted into the liquid media could exert a proportional antioxidant effect. Finally, the resulting solutions were subjected to liquid chromatography–mass spectrometry, to characterise the polyphenolic substances implicated.

2. Materials and methods

2.1. Chemicals and reagents

All solvents used for chromatographic purposes were HPLC grade. Folin–Ciocalteu reagent was from Fluka (Steinheim, Germany). Trolox[®], gallic acid, ellagic acid,

Table 1
Kinetic parameters of polyphenol diffusion from oak chips into model matrices, determined after non-linear correlation of total polyphenol (TP) concentration as a function of time (*t*)

Equation: $[TP] = at^b$			
Matrix	<i>a</i>	<i>b</i>	<i>r</i> ²
Water	72.41	0.380	0.93
12% Ethanol	52.57	0.432	0.94
12% Ethanol, pH 3.4	49.41	0.416	0.89
55% Ethanol	58.26	0.465	0.96

Correlations were established at a 99.99% significance level.

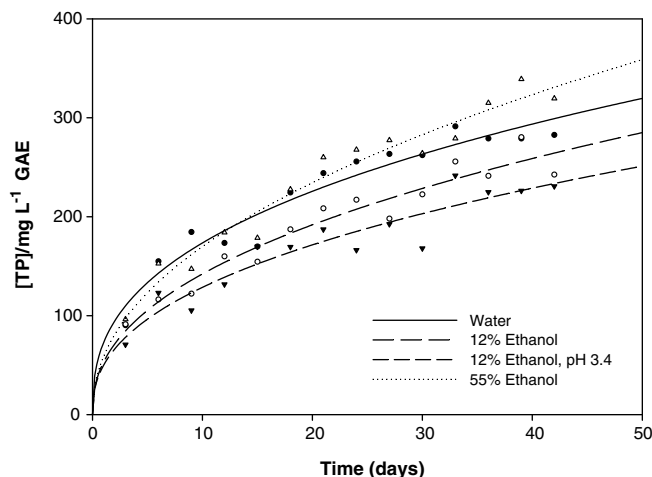


Fig. 1. Kinetics of polyphenol diffusion from oak chips into model matrices. Total polyphenol concentration is expressed as mg l^{-1} gallic acid equivalents (GAE).

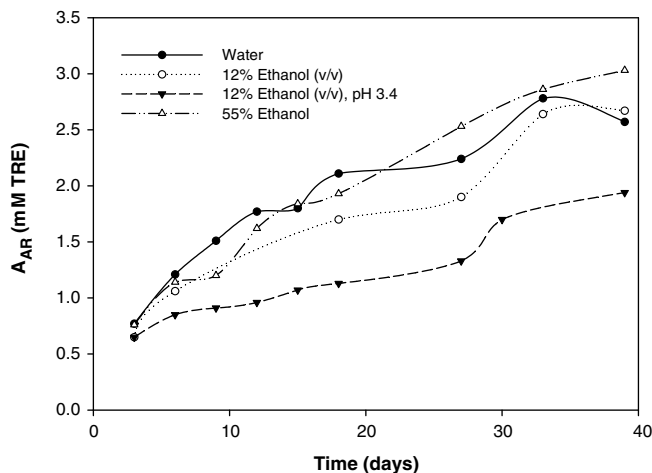


Fig. 2. Evolution of the *in vitro* antiradical activity (A_{AR}) in model matrices containing oak chips. Values are expressed as mM Trolox equivalents (TRE).

and 2,2-diphenylpicrylhydrazyl (DPPH[•]) stable radical were from Sigma Chemical Co. (St. Louis, MO).

2.2. Liquid model matrices and sampling

The liquid model matrices used were distilled water, 12% (v/v) ethanol, 12% (v/v) ethanol containing 6 g l^{-1} sodium potassium tartrate, adjusted to pH 3.4 with HCl, and 55% (v/v) ethanol. Each matrix (500 ml) was placed in 1000-ml glass vials with plastic, air-tight stoppers, and oak chips were added. Chips, kindly donated from the Department of Oenology and Beverage Technology (T.E.I. of Athens), were from French oak (*Quercus petraea*), had undergone no thermal treatment (toasting), with approximate dimensions of $3.45 \text{ cm} \times 2.07 \text{ cm} \times 0.94 \text{ cm}$. Chips were added to each model matrix at 8 g l^{-1} , and solutions were stored at ambient temperature ($22 \pm 2 \text{ }^\circ\text{C}$), in the dark. Sampling was accomplished on a 3-days interval basis. All solutions were

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