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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.

Keywords: Antiradical activity; Antioxidants; Hydrolysable tannins; Model systems; Oak chips

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 hydroalcoholic 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, and 2,2-diphenylpicrylhydrazyl (DPPH·) stable radical were from Sigma Chemical Co. (St. Louis, MO).

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	a	b	r^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.

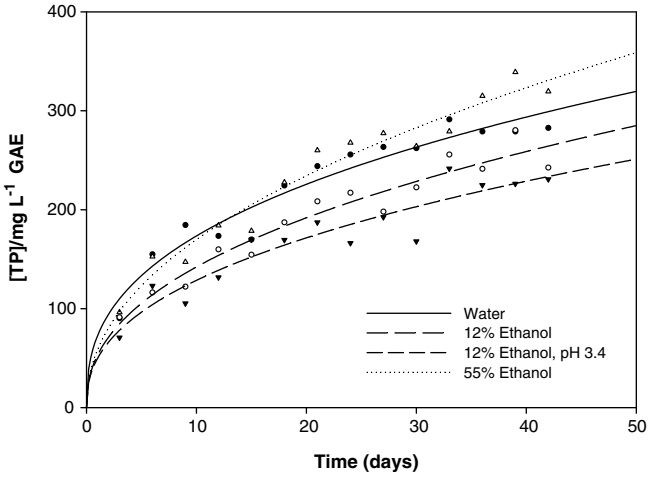


Fig. 1. Kinetics of polyphenol diffusion from oak chips into model matrices. Total polyphenol concentration is expressed as mg l^{-1} gallic acid equivalents (GAE).

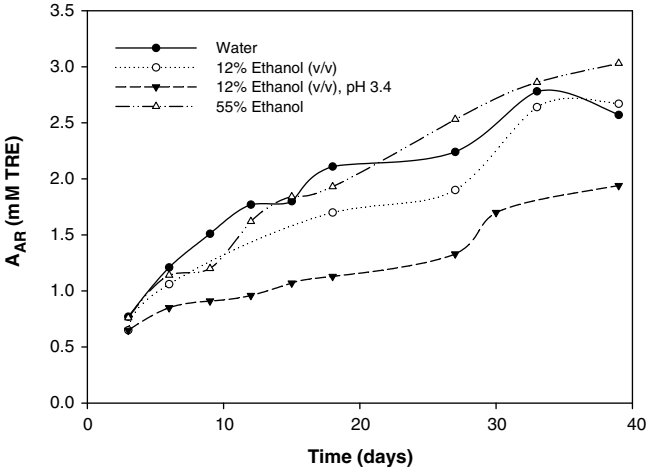


Fig. 2. Evolution of the *in vitro* antiradical activity (A_{AR}) in model matrices containing oak chips. Values are expressed as mM Trolox equivalents (TRE).

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 petrae*), had undergone no thermal treatment (toasting), with approximate dimensions of 3.45 cm × 2.07 cm × 0.94 cm. Chips were added to each model matrix at 8 g l^{-1}, and solutions were stored at ambient temperature (22 ± 2 °C), in the dark. Sampling was accomplished on a 3-days interval basis. All solutions were

Table 2
Correlation of TP concentration with A_{AR} in model matrices, as assessed by linear regression analysis

Matrix	Statistical parameters	
	r^2	Slope
Water	0.88	0.0980
12% Ethanol	0.89	0.0104
12% Ethanol, pH 3.4	0.76	0.0930
55% Ethanol	0.91	0.0950

Correlations were established at a 99.9% significance level.

shaken well prior to every sampling, to ensure withdrawal of uniform aliquots. The total period of each treatment was 42 days.

2.3. HPLC-DAD analysis

All samples were filtered through 0.45-μm syringe filters before chromatographic analysis. The equipment utilised was an HP 1090 series II liquid chromatograph, coupled with an HP 1090 diode array detector and controlled by Agilent ChemStation software. The column was a LiChrosphere RP18, 5 μm, 250 × 4 mm (Merck, Darmstadt, Germany), protected by a guard column packed with the same material. Both columns were maintained at 40 °C. Eluent **A** and eluent **B** were 1% aqueous formic acid and acetonitrite, respectively. The flow rate was 1 ml min^{-1} and the elution programme used was as follows: 0–5 min, 3% **B**; 5–40 min, 35% **B**; 40–50 min, 100% **B**, 50–65 min, 100% **B**. Monitoring of the eluate was performed at 275 nm.

2.4. Liquid chromatography–mass spectrometry

A Finnigan MAT Spectra System P4000 pump was used, coupled with a UV6000LP diode array detector and a Finnigan AQA mass spectrometer. Analyses were carried out on a Superspher 100-4 RP18, 125 × 2 mm, 4 μm, column (Macherey-Nagel, GmbH & Co., KG, Duren, Germany), protected by a guard column packed with the same material, and maintained at 40 °C. Analyses were carried out using electrospray ionisation (ESI) in positive ion mode, with acquisition set at 12 and 50 eV, capillary voltage 3.5 kV, source voltage 45 V, detector voltage 650 V and probe temperature 350 °C. Negative ionisation mode analyses were also ran under the same set of conditions. Chromatographic parameters were as for the HPLC analyses, except that the flow rate was 0.33 ml min^{-1}.

2.5. Determinations

2.5.1. Total polyphenols (TP)

Analysis was carried out using Folin–Ciocalteu methodology, as described previously (Arnous, Makris, & Kefalas,

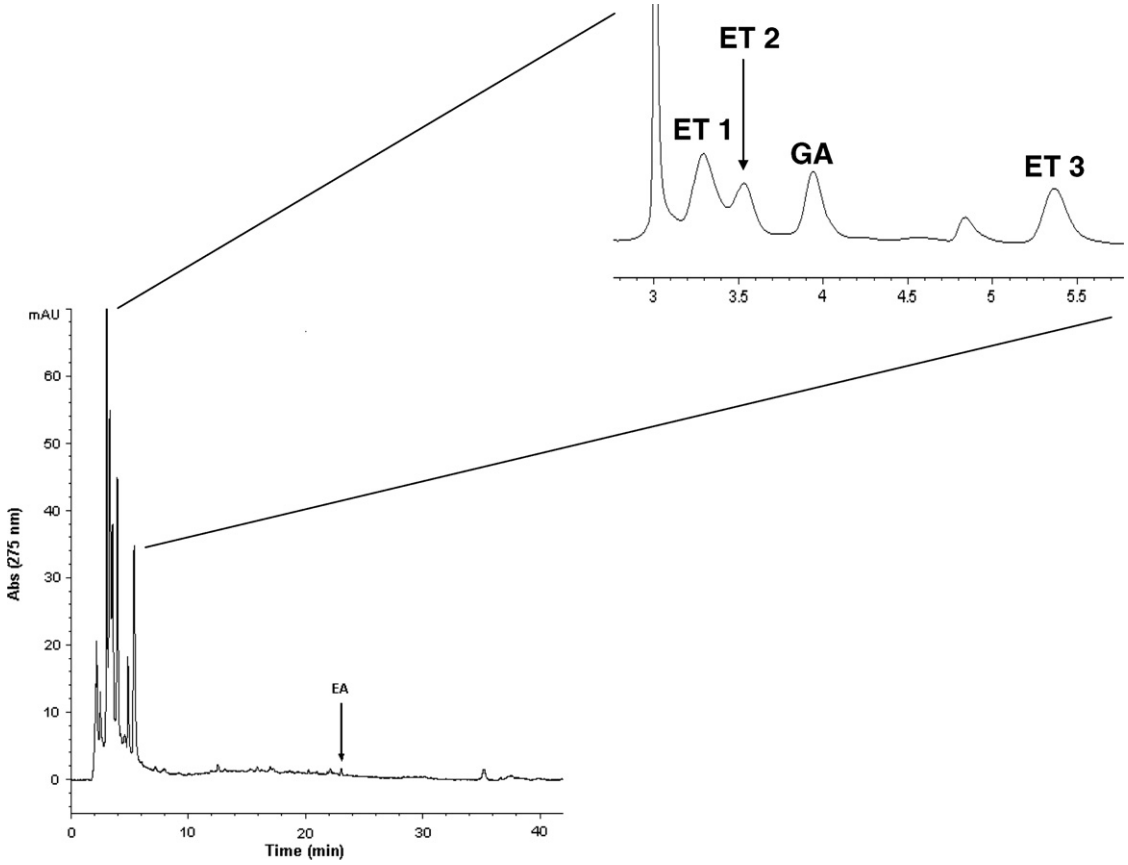


Fig. 3. HPLC trace of the model matrix composed of distilled water, after contact with oak chips for 42 days. Tentative peak assignment: ET1, grandinin or roburin E; ET2, vescalagin; GA, gallic acid; ET3, castalagin; EA, ellagic acid.

2002). Results were expressed as mg l^{-1} gallic acid equivalents (GAE).

2.5.2. Antiradical activity (A_{AR})

A procedure previously reported (Arnous et al., 2002) was employed. Briefly, appropriately diluted sample (0.025 ml) was added to 0.975 ml DPPH$^{\cdot}$ solution (120 μM in methanol), and the absorbance was read at $t = 0$ ($A_{515}^{t=0}$) and $t = 30$ min ($A_{515}^{t=30}$). Results were expressed as Trolox® equivalents (mM TRE), using the following equation:

$$A_{AR} = ((0.021 \times \Delta A_{515}) - 0.038) \times F_D$$

as determined from linear regression, after plotting $\%\Delta A_{515}$ of known solutions of Trolox® against concentration; where $\%\Delta A_{515} = \left(\frac{A_{515}^{t=0} - A_{515}^{t=30}}{A_{515}^{t=0}} \times 100\right)$, and F_D the dilution factor.

2.6. Statistical handling of experimental data

Two replicates were run for each model matrix. All analyses were carried out at least in triplicate, unless otherwise specified, and values were averaged and given, along with the standard deviation. Linear correlations between total polyphenol concentration and antiradical activity were measured at the 99.9% significance level, using simple linear regression. Non-linear fitting of the data from the total polyphenol concentration as a function of time were measured at the 99.99% significance level, using non-linear regression. All statistics were accomplished using SigmaPlot™ 9.0 (Aspire Software International, Ashburn, VA).

3. Results

3.1. Kinetics

Non-linear regression of TP values with time yielded a correlation that obeyed a second order parameter power equation (Table 1). This kinetic approach produced a satisfactory fit of the data, as judged by the square correlation coefficients (r^2), which varied from 0.89 to 0.96. The significance for all correlations established was found to be very high ($p < 0.0001$). The application of this model suggested that migration of phenolics from the chips occurred at a faster rate when only distilled water was used as the liquid system, up to the 12th day (Fig. 1). The diffusion rate thereafter was higher in the liquid matrix composed of 55% (v/v) ethanol. For the whole duration of the process, rates were always slower in matrices composed of 12% (v/v) ethanol or 12% (v/v) ethanol at pH 3.4.

3.2. Antiradical activity (A_{AR})

The A_{AR} of all matrices exhibited a progressive increase throughout the whole duration of treatments (Fig. 2). The rate of augmentation was faster in the solution composed of 55% ethanol, whereas the 12% ethanolic solution with pH 3.4 showed the lowest A_{AR} values. Simple linear regression analysis of total polyphenol concentration with A_{AR} yielded correlations that were statistically significant (Table 2), indicating that leaching of phenolics provoked a proportional antioxidant effect.

3.3. Characterisation of the polyphenolic profile

The model matrices containing the oak chips were subjected to chromatographic analysis, after 42 days of

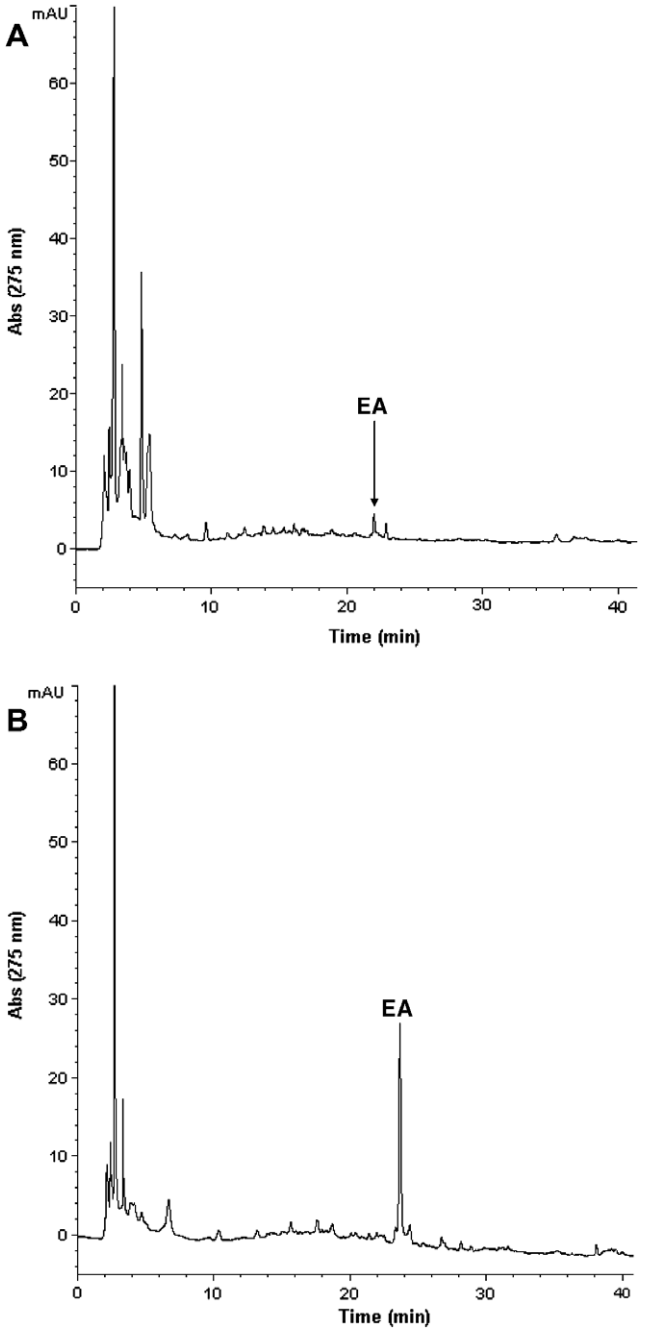


Fig. 4. Chromatograms of solutions of 12% (v/v) ethanol (A) and 12% (v/v) at pH 3.4 (B) containing oak chips, after 42 days. For peak assignment see Fig. 3.

treatment. In the matrix composed of only distilled water, apart from gallic acid, 3 other major phenolics were detected that eluted very early, an evidence of their high polarity (Fig. 3). These peaks were labelled ET1, 2 and 3.

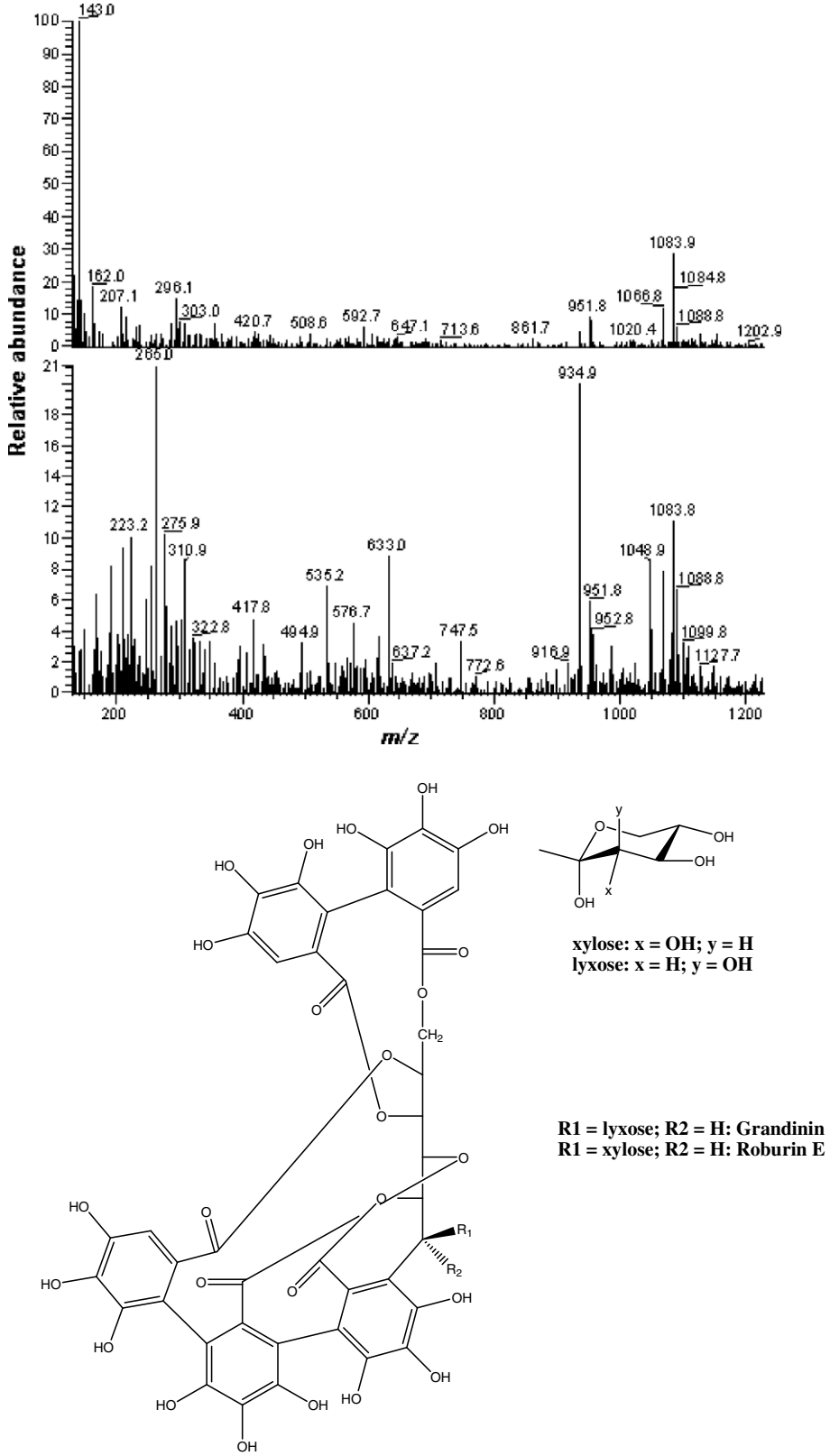


Fig. 5. Mass spectrum of peak assigned as ET1, obtained in positive ion mode, and the structures of grandinin and roburin E. Upper and lower mass spectra were obtained with 12 and 50 eV CID collision energies, respectively.

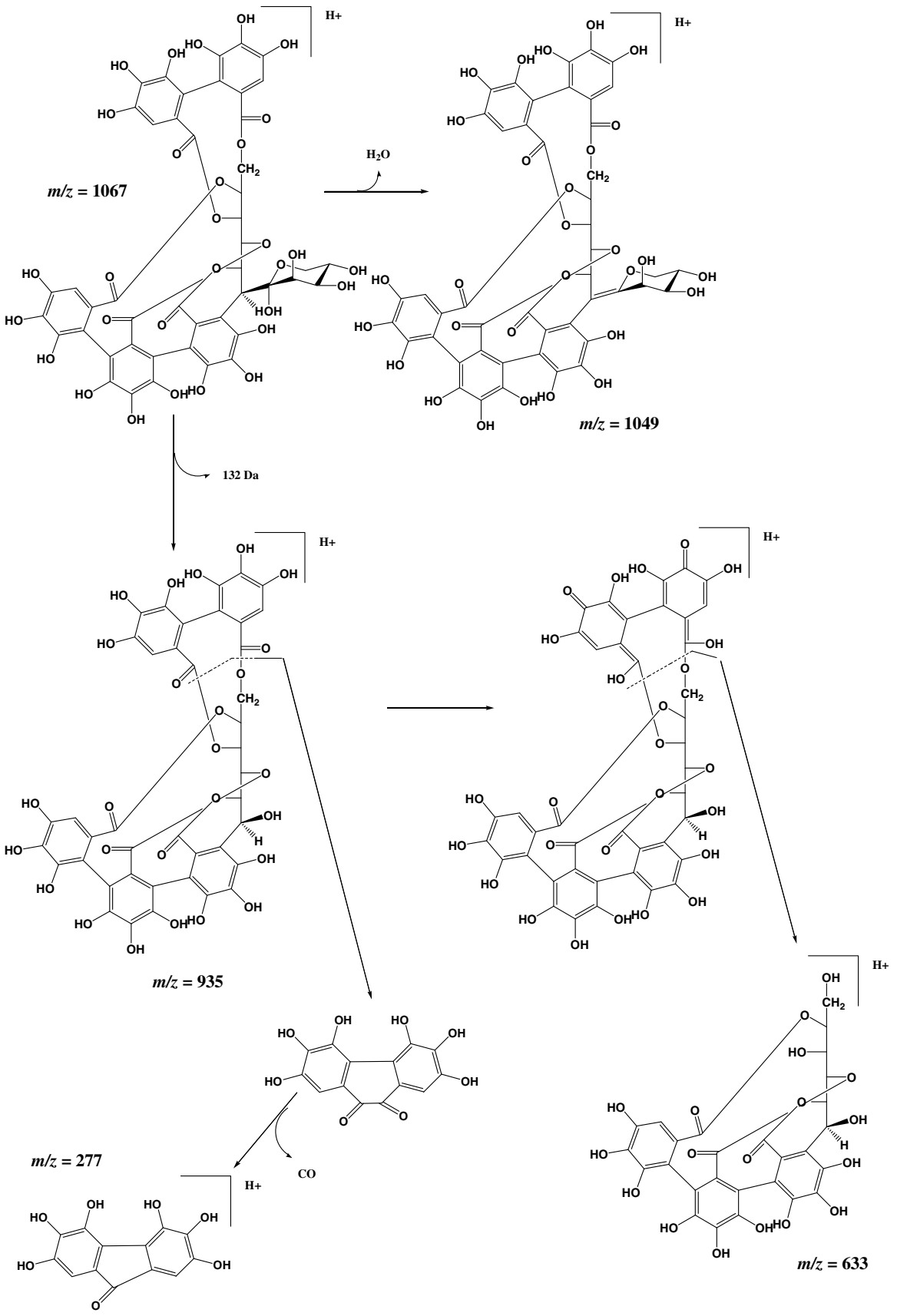


Fig. 6. Putative fragmentation pattern of the peak tentatively characterised as grandinin or roburin E.

Table 3
UV–vis and ESI-MS data of the compounds detected in model solutions containing oak chips

Peak	λ_{max} (nm)	$[M-H]^-$	$[M+H]^+$	Other ions (m/z)	Compound
ET1	230, 289(s)		1067	1089 $[M+Na]^+$, 1085 $[M+H_2O+H]^+$ 1049 $[M-H_2O+H]^+$, 935 $[M-132+H]^+$ 633 $[M-434+H]^+$, 276 $[M-791+H]^+$	Grandinin or roburin E
ET2	230, 289(s)		935	967 $[M+MeOH+H]^+$, 957 $[M+Na]^+$ 917 $[M-H_2O+H]^+$, 633 $[M-302+H]^+$ 615 $[M-302-H_2O+H]^+$, 337 $[M-598+H]^+$ 277 $[M-658+H]^+$	Vescalagin
ET3	230, 289(s)		935	967 $[M+MeOH+H]^+$, 957 $[M+Na]^+$ 917 $[M-H_2O+H]^+$, 633 $[M-302+H]^+$ 615 $[M-302-H_2O+H]^+$, 337 $[M-598+H]^+$ 277 $[M-658+H]^+$	Castalagin
	253, 304(s), 367	301		603 $[2M-H]^-$	Ellagic acid

The amount of these substances was significantly lower in 12% ethanolic solutions (Fig. 4), but also in the 55% ethanolic matrix. In the latter case, high amounts of ellagic acid were found (Fig. 5), relative to all other solutions.

Liquid chromatography–electrospray ionisation mass spectrometry in positive ion mode revealed that the peak denoted ET1 gave a molecular ion at m/z 1067, an adduct with water at 1085 $[M+H_2O+H]^+$, and an Na^+ adduct at m/z 1089 $[M+Na]^+$ (Fig. 6, upper spectrum; Table 3). At increased collision energy (Fig. 6, lower spectrum), the predominant ion with m/z 935 indicated the loss of a 132 Da unit, which was ascribed to a pentose removal (xylose or lyxose) (Nonier et al., 2005). Rearrangement through quinone formation and subsequent cleavage as shown in Fig. 6, would afford the ion with m/z 633, while the ion with m/z 917 could be due to dehydration (Zywicki, Reemtsma, & Jekel, 2002). On the other hand, direct fragmentation of the deglycosylated compound could produce the ion with m/z 277, after a CO removal. Based on this evidence, this peak was identified as grandinin or roburin E. In a similar fashion, ET2 showed a molecular ion at m/z 935, which was confirmed by a Na^+ adduct at m/z 957 (Fig. 7) and a MeOH adduct at m/z 967 $[M+MeOH+H]^+$ (Fig. 7). The ion with m/z 917 could be attributed to dehydration $[M-H_2O+H]^+$. Dehydration of the fragment at m/z 633, brought about as described previously, could yield the ion with m/z 615. Direct cleavage of the molecular ion (m/z 935) could also produce the fragment with m/z 337 and, after a CO loss, the one with m/z 277. Based on these findings, ET2 was tentatively identified as vescalagin (Fig. 8). ET3 possessed identical spectral characteristics, and was designated as castalagin, which according to the literature, behaves as a less polar vescalagin isomer in a reversed-phase HPLC system (Nonier et al., 2005).

4. Discussion

The kinetic behaviour recorded during diffusion of phenolics from oak chips into liquid matrices could be efficiently described by a second order parameter power equation, which provided the appropriate mathematic background for reliable comparisons. The parameters that were calculated graphically suggested that extraction might be accelerated in systems with higher ethanol concentration. However, that was the case only when comparing the 55% ethanolic solution with either water (0% ethanol) or 12% ethanol. By contrast, leaching was faster in water than in 12% ethanol. Another parameter that significantly influenced the leaching rate was the pH. Addition of tartrate salt at a pH 3.4 was proven inhibitory with regard to polyphenol passage from the chips into the liquid. These results are in accordance with earlier examinations (Puech, 1987). This observation merits a more thorough investigation, as it might be critical in the ageing of beverages. Moreover, questions were raised as to what extent other constituents (e.g., glycerol, organic acids, minerals, etc.) could exert similar effects. As migration of wood constituents might also be facilitated by various factors, i.e., toasting temperature (Marinov et al., 1997; Matricardi & Waterhouse, 1999), agitation (Patrício, Canas, & Belchior, 2005), etc., comparative examinations, based on the mathematic model developed, could contribute towards the implementation of the most appropriate conditions for optimal ageing.

The monitoring of the antiradical activity throughout the treatments showed that as polyphenols leached into the solutions, they induced a proportionally elevated antioxidant environment. Although important compositional changes were seen, as judged by the different chromatographic profiles, generally higher A_{AR} values were measured in the solutions where total polyphenol concentration was higher (Fig. 2). It appears therefore that the antiradical ability is directly correlated with the total amount of phenolics, as also demonstrated by the regression analysis (Table 2). However, an integrated, multilateral assessment of this issue would require a more thorough testing on more than one system. Nevertheless, it can be postulated that similar treatments could enrich white wines or distillates, whose polyphenolic concentrations are rather low, in phenolics with appreciable

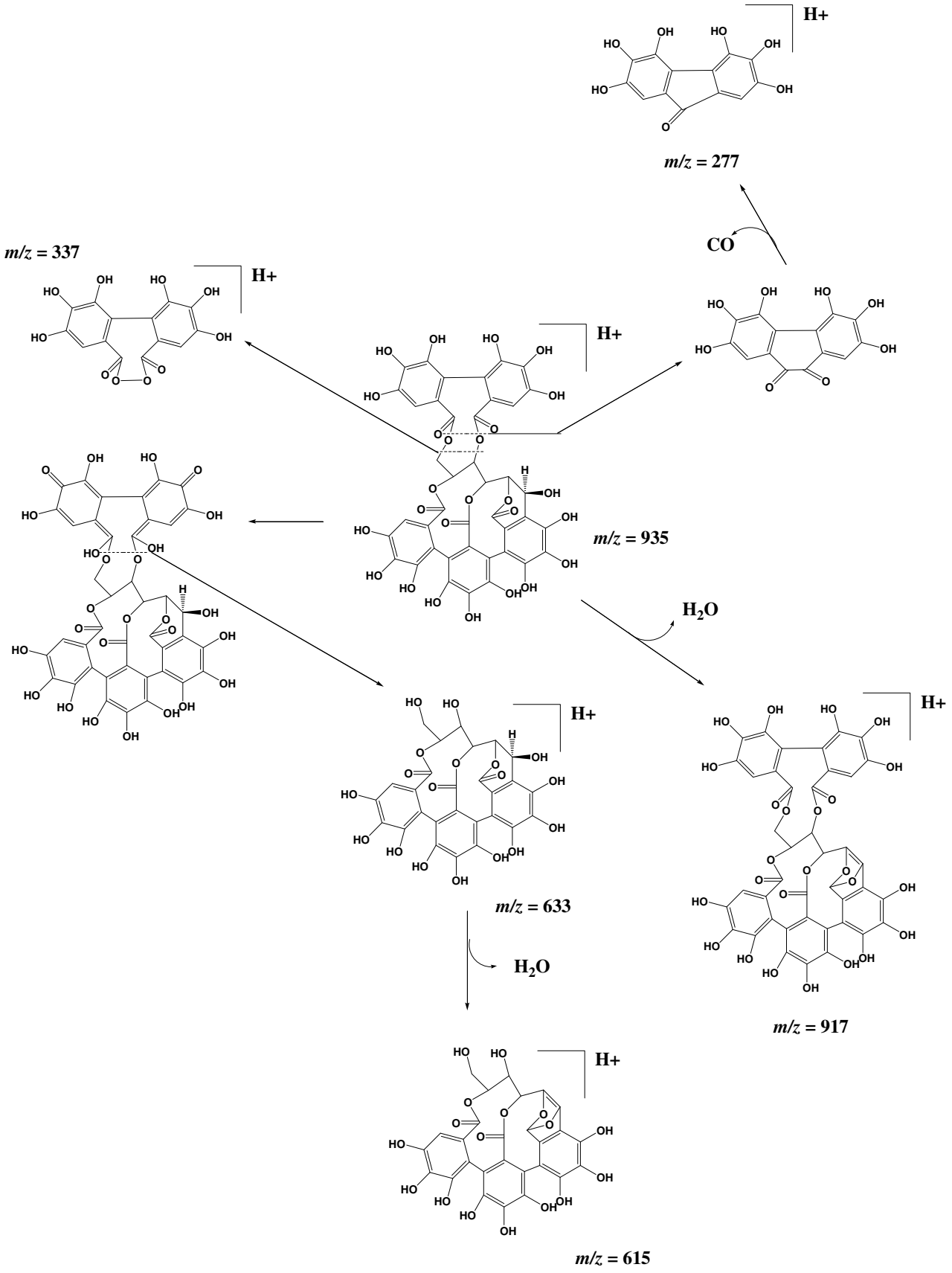
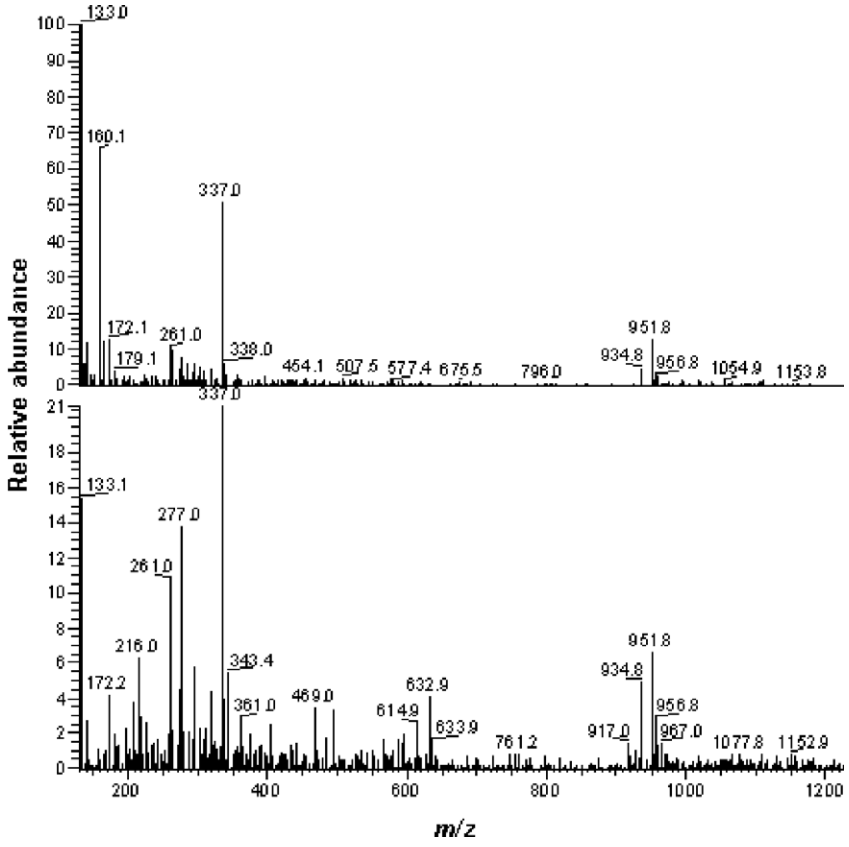
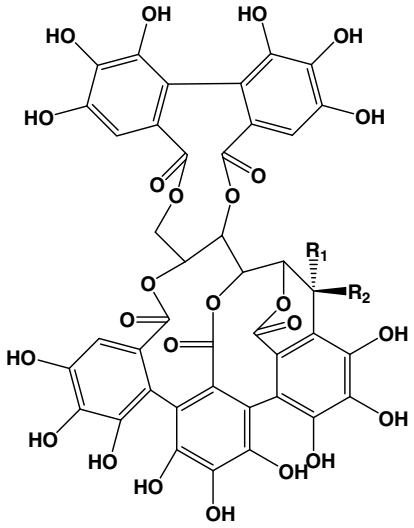


Fig. 7. Mass spectrum of the peak assigned as ET2, obtained in positive ion mode, and the structures of vescalagin and castalagin. Upper and lower mass spectra were obtained with 12 and 50 eV CID collision energies, respectively.





R_1 = H; R_2 = OH: Vescalagin
R_1 = OH; R_2 = O: Castalagin

Fig. 8. Putative fragmentation pathway proposed for the peak tentatively characterised as vescalagin.

antioxidant capacity. On the other hand, the qualitative aspects of the expression of antiradical activity should be stressed, since not all compounds have the same antioxidant properties. Different ageing periods of spirits in oak barrels have been shown to result in varying degrees of ellagitannin hydrolysis, yielding ellagic acid and other derivatives (Viriot, Scalbert, Lapierre, & Moutounet, 1993). Synergistic and/or antagonistic phenomena among these compounds result in an unpredictable outcome.

The HPLC, and LC–MS analyses revealed that the major polyphenols occurring in the matrices treated with oak chips were ellagitannins, as well as some compounds that can derive from ellagitannins after hydrolysis, such as gallic and ellagic acids. In the aqueous matrix, these

compounds might accumulate at relatively higher concentration (Fig. 3), but increased ethanol concentration could contribute to faster hydrolysis, as can be presumed by the increased ellagic acid levels in the 55% ethanolic solution (Fig. 4B). This observation is also corroborated by previously published data (Puech et al., 1999), where castalagin and vescalagin were shown to undergo faster transformations at higher ethanol levels.

Recent studies illustrated possible pathways of ellagitannin metabolism, which are expected to further elucidate the bioavailability of these phytochemicals (Cerdá, Tomás-Barberán, & Espín, 2005). Given the significance of dietary hydrolysable tannins, such as those reported herein, which lies mainly in their antioxidant and other biological properties (Haslam, 1996), enrichment of food systems, such as wines and spirits, in ellagitannins and hydrolysis products thereof, may provide an additional means of delivering dietary antioxidants.

5. Conclusions

With regard to the experimental evidence presented herein, it is proposed that the phenomena underlying migration of certain polyphenols from oak chips into model solutions can be effectively described by implementation of an appropriate mathematic approach. With polyphenol extraction from the wood into the liquid matrix being dependent on time as a function of two parameters, future examinations should aim at clarifying what conditions are likely to affect these parameters. This could lead to a more controlled regulation of ageing, thus allowing for optimisation of the process with regard to time required to achieve the desired quality, in terms of ameliorating both the sensory and nutritional characteristics of wines, at minimal cost. It would be reasonable to assume that the kinetic behaviour of polyphenol leaching in complex matrices such as wines may vary, owing to the complexity of their composition, but this hypothesis remains to be elucidated.

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