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Carbohydrate Polymers 56 (2004) 287–293

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Occurrence of furfuraldehydes during the processing of *Quercus suber* L. cork. Simultaneous determination of furfural, 5-hydroxymethylfurfural and 5-methylfurfural and their relation with cork polysaccharides

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Received 7 August 2003; received in revised 6 November 2003; accepted 20 November 2003

Abstract

A spectrophotometric method was used for simultaneous determination of furfural (F), hydroxymethylfurfural (HMF) and methylfurfural (MF) based on the calculation of the derivative of the spectrum of absorption of the products of their reaction with 2-thiobarbituric acid. This methodology was applied to cork samples obtained from different industrial processing steps for stopper production: cork before autoclaving (BA), cork submitted to one autoclaving procedure (1A), cork 1A washed (1AW) and cork 1A washed and dried (1AWD). The content of furfuraldehydes in cork samples depends on the effect of heat treatments during processing. The formation of F in the autoclaving procedure might be due to the degradation of unbound or cell wall loosely bound pentoses, such as xylose and arabinose. The lower relative amount of fucose and rhamnose is in accordance with the low values determined for MF, and the higher amount of HMF in relation to F showed that the cellulose should also be attacked. In order to minimize the amount of furfuraldehydes in cork stoppers formed by heat treatments, washing and soft drying is necessary. The application of this simple and inexpensive methodology to the cork collected at different manufacturing steps allows controlling the possible thermal abuse of the cork.

Keywords: *Quercus suber* L.; Furfural; 5-Hydroxymethylfurfural; 5-Methylfurfural; Derivative spectrophotometry; Polysaccharides; Industrial processing

1. Introduction

The analytical control of furfuraldehydes is an useful tool in the food and related industries, as the presence of these compounds is very important for the evaluation of the quality of the processing method used and for the organoleptic characteristics of the final product. Furfural (F) and 5-hydroxymethylfurfural (HMF) have been used as potential indicators of temperature abuse and inadequate time of storage in different foods and related materials, such as orange juice (Dinsmore & Nagy, 1974; Espinosa-Mansilla, Salinas, & Nevado, 1992; Marcy & Rouseff, 1984; Meydav & Berk, 1978; Tu et al., 1992), grape juice (Espinosa-Mansilla et al., 1992; Fuleki & Pelayo, 1993), spirits (Granados, Mir, García-Serrada, & López Martinez, 1996; Jeurings & Kuppers, 1980; Mangas, Rodriguez, Moreno, Suárez, & Blanco, 1996), wine and milk (Espinosa-Mansilla et al., 1992), infant milks (Albalá-Hurtado, Veciana-Nogués, Izquierdo-Pulido, & Vidal-Carou, 1997; Albalá-Hurtado, Veciana-Nogués, Mariné-Font, & Vidal Carou, 1998; Ferrer, Alegria, Farré, Albellán, & Romero, 2000), honey (Jeurings & Kuppers, 1980), breakfast cereals (García-Villanova, Guerra-Hernández, Martínez-Goméz, & Montilla, 1993), oral rehydration salt formulations (Tu et al., 1992) beer (Foster II, Samp, & Patino, 2001; Shimizu et al., 2001), and barrel-aged wines (Spillman, Pollnitz, Liacopoulos, Pardon, & Sefton, 1998).

High accumulation of furfuraldehydes, such as F and HMF, indicates that reactions of Maillard type and acid-catalyzed sugar degradation may have taken place and being a potential source of browning in stored foods and other natural products (Espinosa-Mansilla et al., 1992; Tu et al., 1992) and may induce changes on the flavour, colour and textural features of products (Rizi, 1994). The Maillard reaction usually takes place during food processing and/or storage, particularly at high temperatures.

Several techniques have been proposed for the analytical determination of F and HMF. As their occurrence is related

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0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.03.002

with temperature, all methodologies of analysis avoid the use of raise of temperature for extraction improvement. The methods based on spectrophotometry have been used. However, these spectrophotometric methods have in common the handicap of not allowing the distinction between F and HMF. Therefore, a previous separation procedure is needed because of the high overlapping observed in the absorption spectra of both products. Colorimetric methods that include reactions with aniline, with a previous distillation to eliminate HMF have been considered (Dinsmore & Nagy, 1974). Others include the Winkler reaction, that is, the reaction of furfuraldehydes with barbituric acid and *p*-toluidine in acid medium to form a violet product (Espinosa-Mansilla, Durán-Merás, & López, 1996; Tu et al., 1992), or the reaction with 2-tiobarbituric acid (TBA). These methods only allow quantifying the total furfuraldehydes (Tu et al., 1992 and included references). The simultaneous determination of F and HMF in mixtures was also proposed by high-performance liquid chromatography (Albalá-Hurtado et al., 1997, 1998; Lee, Rouseff, & Nagy, 1986; Shimizu et al., 2001), however, previous sample treatments are necessary.

Espinosa-Mansilla et al. (1992) have simultaneously determined F and HMF in orange and grape juices, without any previous handling of the samples, based on the calculation of the derivative of the absorption spectrum of the Winkler reaction products. Tu et al. (1992) used a similar methodology for the analysis of the furfuraldehydes reaction products with TBA. Derivative spectrophotometry offers the advantage of a higher selectivity than conventional spectrophotometry, as overlapping spectra can be resolved by this technique. In addition, in many instances, a previous clarification of the samples is not necessary because the absorption signal due to the turbidity is avoided by the derivative approach, which simplifies the method (Tu et al., 1992). This simultaneous colorimetric analysis allowed the development of a stopped-flow method for semiautomatic determination of furfuraldeydes in foods and pharmaceuticals (Espinosa-Mansilla, Muñoz de la Peña, & Salinas, 1993), which shows that derivative spectrophotometry can be an interesting methodology for industrial quality control.

During the industrial processing of cork for stopper production, the cork is submitted to several thermal treatments, such as boiling, autoclaving and/or drying procedures. These treatments involve temperatures in the range 80–130 °C, however, to our knowledge, no data are available about the fate of the cork components susceptible of thermal degradation, namely the cell wall polysaccharides and other carbohydrates which can favour the production of furfuraldehydes in cork during processing. Furthermore, the chemical analyses carried out on corks supplied from different industrial steps indicate that the autoclaving procedure degrades, in some extension, the carbohydrates. The corresponding cork samples show the presence of a mixture of F, HMF and 5-methylfurfural (MF) (Rocha, 1997).

Two aims were established in this work. The first aim was to develop a derivative spectrophotometric method for simultaneous determination of F, HMF and MF based of the TBA reaction. This was applied to cork samples obtained from different industrial processing steps: cork before autoclaving (BA), cork submitted to one autoclaving procedure (1A), cork 1A washed (1AW) and cork 1A washed and dried (1AWD). The second aim of the work was to study, for the first time, the relation between the amount and the type of furfuraldehydes detected and the polysaccharides of the cork cell wall and the carbohydrates not integrated in the cork cell wall, extracted with ethanol/water solutions. The establishment of a relation between furfuraldehydes and their origin will allow their use as diagnostic markers for the evaluation of cork cell wall integrity, and as a tool to follow their changes during processing.

2. Material and methods

2.1. Chemicals

Furfural (F), 5-methylfurfural (MF) and 5-hydroxymethylfurfural (HMF) were obtained from Sigma Chemical Co. (St Louis, MO).

2.2. Plant material

Reproduction cork from *Quercus suber* L. was used. All the phloem and pheloderm tissues from the outer surface of cork were removed. In these assays, the cork samples studied were obtained from different manufacturing steps: cork without autoclaving procedure (BA), cork submitted to one (1A) autoclaving procedure (the cork slabs were autoclaved with water vapour for 18–20 min, at 130 °C at a pressure of 180 kPa), cork 1A washed with water (1AW), and cork 1A washed and dried for 1 h, at 80–90 °C (1AWD), in accordance with the procedures used in the supplying cork stoppers industry. All treatments were carried out in the factory. Of each type of cork, ca. 40–46 samples were analysed.

2.3. Standards

In order to validate the method, standard solutions of furfural (0.58 mg/l ethanol), 5-hydroxymethylfurfural (0.50 mg/l ethanol) and 5-methylfurfural (0.45 mg/l ethanol) were prepared, from which ternary mixtures of different concentrations were made: 0.91–7.82 mg/ml for F, 0.76–6.54 mg/ml for HMF, and 0.89–7.62 mg/ml for MF (Table 1).

2.4. Furfuraldehydes extraction procedure

The applicability of the method was tested on several cork samples selected to include a variety of thermal treatments. The cork samples (ca. 15 g) were cut into pieces

Table 1
Statistical data for calibration curves

Compound	Regression equation	Cor. coefficient[a]	Conc. range[b]
F, at 440 nm I/D[c]	$d_{F,440} = 0.0029 - 0.0029C_F{}^d \pm 0.0001/\pm 0.0002$	0.9998	0.91–7.82
F, at 435 nm I/D[c]	$d_{F,435} = 0.0071 - 0.0047C_F{}^d \pm 0.0003/\pm 0.0003$	0.9998	0.91–7.82
HMF, at 440 nm I/D[c]	$d_{HMF,440} = 0.0027 - 0.0019C_{HMF}{}^d \pm 0.0002/\pm 0.0003$	0.9994	0.76–6.54
HMF, at 414 nm I/D[c]	$d_{HMF,414} = 0.0021 + 0.0016C_{HMF}{}^d \pm 0.0002/\pm 0.0002$	0.9994	0.76–6.54
MF, at 435 nm I/D[c]	$d_{MF,435} = 0.0024 + 0.0046C_{MF}{}^d \pm 0.0001/\pm 0.0002$	0.9998	0.89–7.62
MF, at 414 nm I/D[c]	$d_{MF,414} = 0.0043 + 0.0042C_{MF}{}^d \pm 0.0003/\pm 0.0004$	0.9996	0.89–7.62

[a] Correlation coefficient ($n = 8$).
[b] Concentration range (mg/ml).
[c] Confidence interval of the I (bias) and D (slope) at 95%.
[d] Compound concentration.

of about 2 cm × 2 cm and were introduced in a 250 ml flask containing 130 ml of ethanol.

In order to study the influence of the time of extraction, furfuraldehydes were extracted from cork samples (1A, 1AW, 1AWD), submerged in ethanol, at room temperature. After 1, 2, 4 and 6 months, the ethanolic extract was separated from the cork sample by filtration, and analysed.

2.5. Reaction with 2-thiobarbituric acid (TBA)

In a 25 ml volumetric flask was introduced 5 ml of the ethanolic cork extract or ternary mixtures of standards, followed by 8.5 ml of concentrated hydrochloric acid and 7.0 ml of 30 mM TBA solution (Tu et al., 1992). The samples were heated to 40 °C for 30 min, allowed to cool to 20 °C, and diluted to the mark with water.

2.6. Absorption spectra in the visible

Absorption spectra were acquired between 550 and 300 nm, against a solution containing distilled water and 8.5 ml of concentrated hydrochloric acid. The analyses were carried out in a double beam UV/VIS Spectrophotometer Varian DMS 300.

2.7. First derivative of the absorption spectra

The derivatives were calculated digitally by the spectrophotometer microprocessor DMS 300, with an acquisition speed of 200 nm/min and a resolution of 4 nm. The determination of the first derivative (*d*) was carried out in the wavelengths corresponding to the maxima of absorption of the TBA reaction products with F, HMF and MF, at 414, 435 and 440 nm, respectively.

2.8. Preparation of the polysaccharides of cork cell wall (CP) and the carbohydrates not integrated in the cork cell wall (EW)

Cork BA was manually ground to a fine powder (60 mesh). The cork was submitted to a sequence of treatments in order to obtain the polysaccharide fraction according to Pereira (1988). The cork powder (5.5 g) was extracted in a soxhlet apparatus, successively with dichloromethane (8 h), ethanol (8 h) and water (8 h). The extractive-free cork material was treated with 3% $NaOCH_3$ in methanol for 6 h under reflux to remove the suberin, and then was extracted 1 h at 20 °C with dioxan. The remaining residue, containing the cork polysaccharides (CP) was freeze-dried for analysis.

Ground cork BA (15 g) was also macerated in 12% ethanolic solution (130 ml) for 6 months. The extract (six replicates) was concentrated under reduced pressure by rotary evaporation at 37 °C and the residue obtained from this ethanol/water solution (EW) was freeze-dried for analysis.

2.9. Carbohydrate analysis

Neutral sugars were released by Saeman hydrolysis (Selvendran, March, & Ring, 1979) and analysed as their alditol acetates by gas chromatography (GC) according to Blakeney et al. (Blakeney, Harris, Henry, & Stone, 1983) and Harris et al. (Harris, Blakeney, Henry, & Stone, 1988). The CP and EW (3–5 mg) were treated with 72% H_2SO_4 at room temperature for 3 h, followed by 1 M H_2SO_4 at 100 °C for 2.5 h (after 1 h, 0.5 ml of the hydrolysate was removed for uronic acid determination). The acid hydrolysate was cooled and an internal standard (2-deoxy-glucose, 1 mg/ml, 200 μl) was added. This solution (1 ml) was then neutralized with 200 μl of solution of 25% NH_3 and the sugars were reduced with 100 μl of 15% $NaBH_4$ in 3 M NH_3 (30 °C, 30 min); the reaction was stopped by two additions of 50 μl of acetic acid. An aliquot (0.3 ml) of this solution was treated with 1-methylimidazole (0.45 ml) and acetic anhydride (3 ml) for 30 min at 30 °C. This solution was then treated with water (3 ml) to decompose the excess of acetic anhydride and the acetylated sugars were extracted with dichloromethane (3–5 ml). The dichloromethane phase was washed three times with water and evaporated to dryness. The alditol acetates were dissolved in dichloromethane (70 μl) and analysed by GC using a Hewlett-Packard 5890 equipped with split injector (split ratio 1:60) and FID detector. A 25 m column CP-Sil-43 CB, with ID 0.15 mm and 0.20 μm film thickness was used. With the injector and detector operating at 220 °C, the following temperature program was used: 180 °C for 5 min and 200 °C for 20 min, with a rate of 0.5 °C/min. Linear velocity of the carrier gas (H_2) was set at 50 cm/s at 200 °C.

Uronic acids were determined colorimetrically by a modification (Coimbra, Delgadillo, Waldron, & Selvendran, 1996) of the method of Blumenkrantz and Asboe-Hansen (Blumenkrantz & Asboe-Hansen, 1973). The aliquot of 0.5 ml of hydrolysate previously removed from the neutral sugars determination was filtered through a GF/C filter and diluted four times with water. To 3 ml of ice-cold concentrated sulphuric acid containing 50 mM boric acid, 0.5 ml of sample solution was added, mixed and heated in a boiling water bath for 10 min. After cooling, 100 μl of *m*-phenyl-phenol (0.15% in 0.5% NaOH) was added and the solution was allowed to stand in the dark for 30 min to develop the pink-red colour; the absorbance was read at 520 nm. Standards were made with galacturonic acid, with a linear correlation from 0 to 40 μg of uronic acid in the tube.

3. Results and discussion

3.1. Absorption spectra in the visible

The method of TBA consists of the reaction of TBA with the furfuraldehydes in acidic medium (Tu et al., 1992). The products of reaction of the F, HMF and MF with TBA present a yellow coloration and absorb in the visible region, with maxima at 414, 435 and 440 nm, respectively (Fig. 1). The bands of absorption of each compound are wide and strongly overlapped. When these three compounds are present simultaneously, it was observed only one band (M) corresponding to the overlapping of the bands of absorption of each one of them (Fig. 1), which excludes the possibility of its simultaneous determination by the conventional spectrophotometric method. Derivative spectrophotometry was used for resolving these ternary mixtures.

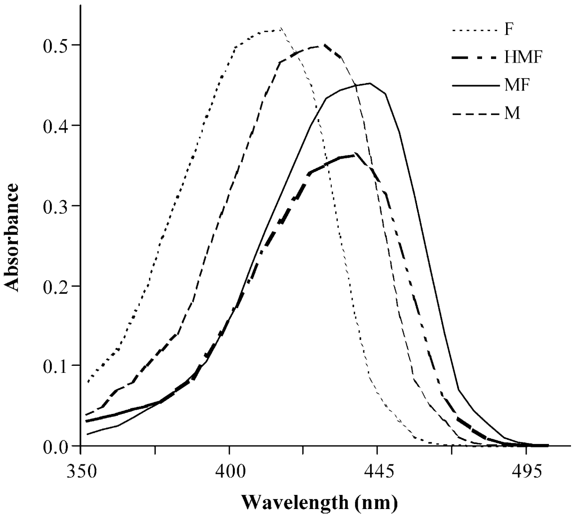

Fig. 1. Absorption spectra of the products of reaction of TBA with furfural (F), hydroxymethylfurfural (HMF), methylfurfural (MF) and with a mixture of the three compounds (M).

3.2. First derivative of the absorption spectra

Fig. 2 shows the first derivative of the absorption spectra of the products formed by reaction of F, HMF, and MF with TBA. The zero-crossing-points were used to define the wavelengths where the derivate of the absorbance is proportional to the concentration of F, HMF and MF and, therefore, the wavelengths suitable for preparation of the calibration graphs (Tu et al., 1992). The contribution of one compound, where its derivative is zero, is null, having only the contribution of the other two compounds. The zero-crossing-points for F, HMF and MF were 414, 435 and 440 nm, respectively. In Fig. 2, it is observed that, for the zero of F, at 414 nm, the contributions of HMF and MF ($d_{\mathrm{HMF},414} + d_{\mathrm{MF},414}$) can be measured (system I). For the zero of HMF, at 435 nm, the contributions of F and MF ($d_{\mathrm{F},435} + d_{\mathrm{MF},435}$), and for the zero of MF, at 440 nm, the contributions of F and HMF ($d_{\mathrm{F},440} + d_{\mathrm{HMF},440}$), can be measured

$$\text{System I}\qquad \begin{cases} d_{414} = d_{\mathrm{HMF},414} + d_{\mathrm{MF},414} \\ d_{435} = d_{\mathrm{F},435} + d_{\mathrm{MF},435} \\ d_{440} = d_{\mathrm{F},440} + d_{\mathrm{HMF},440} \end{cases}$$

By the use of standard solutions of F, HMF and MF, the calibration curves for measurements of the derivative absorbance at 435 and 440 nm for F, 414 and 440 nm for HMF, and 414 and 435 nm for MF were established (Table 1). The determined values for the coefficients of correlation and the fact of the curves to intercept the abscissas axes near to zero showed a good linearity.

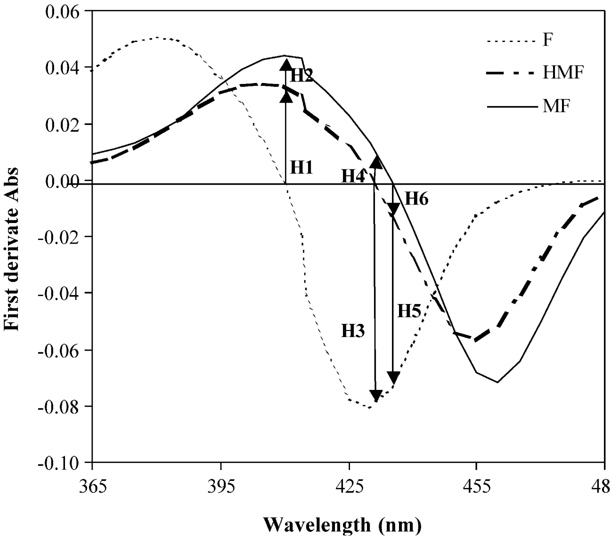

Fig. 2. First-derivative spectra of the products of reaction of TBA with furfural (F), hydroxymethylfurfural (HMF), and methylfurfural (MF). $d_{414} = \mathrm{H}_1 + \mathrm{H}_2$; $d_{435} = \mathrm{H}_3 + \mathrm{H}_4$; $d_{440} = \mathrm{H}_5 + \mathrm{H}_6$.

Table 2
Determination of F, HMF and MF in synthetic mixtures (A–J)

Synthetic mixtures	F[a]			HMF[a]			MF[a]		
	Added	Found	Rec (%)	Added	Found	Rec (%)	Added	Found	Rec (%)
A	0.98	0.89	91	0.79	0.70	88	0.93	0.88	95
B	1.33	1.30	98	1.12	1.07	96	1.77	1.71	97
C	1.82	1.83	101	4.54	4.30	95	2.33	2.34	100
D	1.82	1.80	99	1.52	1.54	101	2.33	2.41	103
F	2.54	2.51	99	2.43	2.39	98	2.85	2.94	103
G	2.73	2.64	98	3.02	3.11	103	3.42	3.27	96
E	2.73	2.76	101	2.43	2.39	98	1.77	1.63	92
H	3.87	3.81	98	1.12	0.98	88	4.67	4.62	99
I	3.87	3.83	99	4.54	4.43	98	4.67	4.62	99
J	5.68	5.82	102	6.78	6.93	102	5.14	5.33	104
Average			99			97			99
Coefficient of variation (%)			3.0			5.2			3.9

[a] Compound concentration (mg/ml).

Substituting the values determined experimentally of d_{414}, d_{435} and d_{440} in the dx, λ equations of system I, where x represents the compound and λ represents the wavenumber, it was possible to determine simultaneously the concentration of F, HMF and MF (C_F, C_{HMF} and C_{MF}) in system III, according to the resolution of system II in order to C_F, C_{HMF} and C_{MF}.

System II

$$\begin{cases} d_{414} = 0.0021 + 0.0016C_{HMF} + 0.0043 + 0.0042C_{MF} \\ d_{435} = 0.0071 - 0.0047C_{CF} + 0.0024 + 0.0046C_{MF} \\ d_{440} = 0.0029 - 0.0029C_F + 0.0027 - 0.0019C_{HMF} \end{cases}$$

System III

$$\begin{cases} C_F = 540.77d_{414} - 1.32 + 455.39d_{440} - 493.75d_{435} \\ C_{HMF} = -287.09d_{435} - 3.41 + 552.53d_{414} + 465.28d_{440} \\ C_{MF} = -1221.38d_{440} + 4.96 - 825.39d_{414} + 753.61d_{435} \end{cases}$$

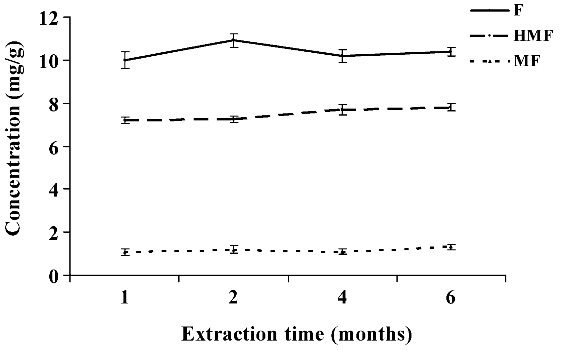

Fig. 3. Variation in the concentration (mg compound/g dry cork) of the furfural (F), hydroxymethylfurfural (HMF) and methylfurfural (MF) in the extracts obtained from cork 1A, using different extraction times (1, 2, 4 and 6 months).

3.3. Determination of furfuraldehydes in ternary mixtures

In order to validate the method, determinations were carried out in ternary mixtures prepared with known concentrations of F, HMF and MF (Table 2). The recovery for F ranged from 91 to 102%, for HMF from 88 to 103%, and for MF from 95 to 104%. Due to the mean high recovery obtained from the three furfuraldehydes (99% for F, 97% for HMF and 99% for MF), and the low standard deviations (3.0% for F, 5.2% for HMF and 3.9% for MF), the results were considered satisfactory.

3.4. Determination of furfuraldehydes in cork samples

In order to determine the shortest time of extraction which correspond to a representative concentration of furfuraldehydes, the cork samples were placed in ethanol for 1, 2, 4 and 6 months. Fig. 3 represents the concentration of F, HMF and MF (mg/g cork) in the ethanolic extracts of an autoclaved cork (1A) for the different extraction times. The amount of F, HMF and MF increased only 4–6% after 6 months of maceration comparatively to 1 month. Similar tendencies were obtained for 1AW and 1AWD cork

Table 3
Results of the determination of F, HMF and MF in cork, data obtained from extraction time of six months

Sample	F[a]	HMF[a]	MF[a]
Cork before autoclaving procedure (BA), $n = 44$	0.11 (7)[b]	0.00 (–)	0.00 (–)
Cork after one autoclaving procedure (1A), $n = 46$	10.24 (4)	7.17 (2)	0.96 (6)
Cork 1A washed (1AW), $n = 40$	7.37 (3)	4.95 (4)	0.67 (5)
Cork 1A washed and dry (1AWD), $n = 40$	4.79 (5)	3.08 (6)	0.43 (9)

[a] mg compound/g dry cork.

[b] Coefficient of variation (%).

Table 4
Sugar composition of polysaccharides of the cork cell wall (PC) and the carbohydrates not integrated in the cork cell wall that are extracted with ethanol/water solutions (EW); $n = 6$

Cork BA	Sugars (mol%)								Total sugars (mg/g)	Sug. (%)[a]
	Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA		
PC	2	*t*[b]	8	30	3	3	42	12	259 (5)[c]	25.9
EW	*t*	*t*	10	53	3	4	17	13	490 (2)[d]	1.43

UA, uronic acid.

[a] Values are expressed as percentage of anhydrosugar in cork.

[b] Trace.

[c] Values are expressed as mg of 'anhydrous sugar'/g dry cork, numbers in parentheses correspond to the coefficient of variation (%).

[d] Values are expressed as mg of 'anhydrous sugar'/g dry residue Rc, numbers in parentheses correspond to the coefficient of variation (%).

samples, which suggest that 1 month of maceration may be adequate for using in future determinations.

The results obtained for the samples collected at the different industrial steps of the cork stoppers production are shown in Table 3. The samples not submitted to the autoclaving procedure (BA) show only traces of F, while the cork autoclaved (1A) exhibits considerable amounts of F and HMF, and traces of MF. These results indicate that the cork furfuraldehydes should be produced because of thermal treatments during the autoclaving procedure. The amount of F, HMF and MF decreased 30% when the cork was washed (1AW), and decreased 55% when it was washed and dried (1AWD). According to the literature (Belitz & Grosch, 1999), F is the principal decomposition product of pentoses, such as xylose and arabinose, and HMF is the main decomposition product of hexoses presenting a $-CH_2OH$ group in C6, such as glucose, galactose and mannose. Based on the same reaction principles, MF is a decomposition product of deoxyhexoses with a $-CH_3$ group in C6, such as fucose and rhamnose.

Table 4 shows that the cork polysaccharides (BA) are composed mainly of glucose (42 mol%), xylose (30%), uronic acid (12%), and arabinose (8%), which represented 26% of cork dry material. Fucose and rhamnose accounted only for 2% of cork polysaccharides. However, the sugars composition of the material not integrated in the cell wall (EW), extracted with a 12% ethanol solution, is different. In EW residue, the major sugar component was xylose (53 mol%), glucose accounted for 17%, uronic acids 13%, and arabinose 10%. Only trace amounts of deoxyhexoses were detected. This EW extract accounted for 3% of cork dry material, which represented only 1.4% of cork sugars. Comparing the sugars composition of PC and EW, it is verified that the amount and the type of furfuraldehydes seem to be related to the chemical composition of EW (Table 4). EW was composed mainly by sugars which thermal degradation produces F (xylose and arabinose). The occurrence of glucose, mannose and galactose in EW also explains the origin of HMF and the traces of fucose and rhamnose explain the detection of MF in small amounts. The ratio of F to HMF producing sugars that potentially can produce furfuraldehydes was 2.6. The accessibility of these sugars to the autoclaving water vapour is higher than that of the cell wall polysaccharides, promoting their degradation. However, the relative proportion of F to HMF in the sample 1A, submitted to thermal treatment, was 1.4. This ratio cannot only be explained by the sugars present in EW extract, but suggests the contribution of the hexoses from PC in the production of furfuraldehydes, meaning that the degradation of cell wall polysaccharides also occurs. Although cell wall glucuronoxylans are more susceptible to thermal degradation than the cellulose (Funaoka, Kako, & Abe, 1990), the relative amount in cork of HMF in relation to F also showed a possible attack of cellulose, the major cork cell wall polysaccharide.

4. Conclusion

The method developed, which comprises the reaction of F, HMF and MF with TBA and the determination of the first derivative of the spectra, allows the simultaneous determination of the three furfuraldehydes.

The results suggest that the formation of F in the autoclaving procedure might be due to the degradation of unbound or cell wall loosely bound pentoses, such as xylose and arabinose. The relative amount of HMF in relation to F showed that the cellulose should also be attacked. The lower relative amount of fucose and rhamnose is in accordance with the low values determined for MF.

The content of furfuraldehydes in cork samples depends on the effect of heat treatments during processing. Thus, in order to minimize the amount of furfuraldehydes in cork stoppers, and consequently in wine, it is suggested that the cork submitted to an autoclaving procedure should be washed and soft dried. The application of this simple and inexpensive methodology allows monitoring the effect of different processing steps during cork stopper production on the amount of furfuraldeydes, allowing to identify possible thermal abuse of the cork.

Acknowledgements

The authors thank the financial support the Research Unit 62/94, Química Orgânica, de Produtos Naturais e Agroalimentares. S.R. also thanks the support of JNICT (BD/1218/91-IF).

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