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# A Fourier transform infrared spectroscopy study of wine polysaccharides

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**Abstract**

Fifteen polysaccharides previously purified from a red wine and whose structures had been characterised were studied by Fourier transform-infrared spectroscopy (FTIR). These polysaccharides are representative of the main families of polysaccharides found in wines: mannoproteins, arabinogalactan-proteins, RG-I and RG-II. The spectra were processed at between 950 and 1850 $cm^{-1}$. Significant differences were found between the polysaccharide families. The spectra are explained with reference to glycosyl residues, proteic and galacturonic acid compositions.
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*Keywords:* FTIR; Wine; Polysaccharides; Arabinogalactan-proteins; Mannoproteins; Rhamnogalacturonan-I; Rhamnogalacturonan-II; RG-II

## 1. Introduction

The polysaccharides in wines are mainly of two sources, originating either in the cell walls of grape berries after degradation by pectic enzymes during berry maturation and the various vinification treatments or in yeast walls during alcoholic fermentation. They form one of the major groups of macromolecules in wines, together with polyphenols and proteins. Wine polysaccharides display great structural diversity and are found at a concentration of 0.2–2 $g\,l^{-1}$. The respective concentrations of these substances in wines depend on numerous parameters including the grape variety, the stage of berry maturity, the vinification method and the treatments of harvested grapes leading to greater, different solubilisation of the macromolecular components of grape berries (Pellerin & Cabanis, 1998).

The largest group from berry cell walls includes Polysaccharides Rich in Arabinose and Galactose (PRAGs) such as the arabinogalactan proteins (AGPs) and arabinans, (Brillouet, Bosso, & Moutounet, 1990; Pellerin, Vidal, Williams, & Brillouet, 1995). The second largest family of polysaccharides originating in grape berry cell walls consists of Rhamnogalacturonan II (RG-II) (Doco & Brillouet, 1993; Pellerin et al., 1996). This is released during the maceration of solids in red wine making. Mannoproteins (MPs) from yeast walls form another large family in wines (150 mg/l) (Llaubères, Dubourdieu, & Villetaz, 1987).

Polysaccharides are involved in many oenological phenomena. The first role awarded to them is their contribution to the mellowness of wines (Semichon, 1927). However, polysaccharides have been studied for several years for reasons of their impact on the organoleptic qualities of wines, in particular because of their ability to interact with polyphenols (Riou, Vernhet, Doco, & Moutounet, 2002), their effect as protective colloids, their contribution to protein stability (Waters, Pellerin, & Brillouet, 1994) and to tartaric stability (Gerbaud, Gabas, Blouin, Pellerin, & Moutounet, 1997; Gerbaud et al., 1996) and also their

*Abbreviations:* ATR, attenuated total reflection; GC–MS, gas chromatography–mass spectroscopy; PCA, principal component analysis; PS, polysaccharides.

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role in the complexing of divalent cations (O'Neill et al., 1996; Pellerin et al., 1997), their role in the persistence of bubbles in sparkling wines, their interaction with aromatic compounds (Chalier, Angot, Delteil, Doco, & Gunata, 2007) and their involvement in filterability and the fouling of filter membranes (Belleville, Brillouet, Tarodo de la Fuente, & Moutounet, 1990; Vernhet, Pellerin, Belleville, Planque, & Moutounet, 1999). It has been demonstrated that the addition of MP fractions extracted from yeast walls using chemical or enzymatic methods inhibits the formation of potassium bitartrate crystals (Moine & Dubourdieu, 1996) and thus stabilises the wine.

The polysaccharide composition of musts and wines is known (Pellerin & Cabanis, 1998) but numerous, very different identification and quantification techniques are used and mentioned in the literature (Vidal, Doco, Moutounet, & Pellerin, 2000). The identification and quantification of the polysaccharides found in wines is therefore an important question. Operations are performed on purified, isolated polysaccharides by analysis of the polysaccharide and monosaccharide composition by GC–MS after acid hydrolysis, reduction and acetylation (Doco, Quellec, & Moutounet, 1999). This method can be considered today as the reference method for the assay of polysaccharides in wine as it enables precise quantification. However, performance is difficult because of the great number of operations that it requires, the know-how that is essential for successful completion of the analysis and the fact that automation is difficult.

Analysis by Fourier transform infrared spectroscopy (FTIR) is a comparatively new method used since the 1990s in the agroindustry sector (Bertrand & Dufour, 2000), with more recent applications in fermented beverages (Fayolle, Picque, Perret, Latrille, & Corrieu, 1996) and wine (Dubernet & Dubernet, 2000; Kupina & Shrikhande, 2003; Patz, David, Thente, Kurbel, & Dietrich, 1999). It has numerous advantages including ease of implementation, the small sample quantity required, speed and the almost complete absence of consumables. Spectral acquisition is performed directly on wine after clarification, filtration or centrifuging. The technique enables the individual quantification of the main compounds found in wine: ethanol, glucose-fructose and organic acids with acceptable accuracy.

Analysis of the quantitatively minor components of wine is more recent. Schneider, Charrier, Moutounet, and Baumes (2004) propose the assay of aroma precursors in grape berries by medium infrared (MIR) analysis after extraction, concentration and purification on resin. With regard to polysaccharides, MIR quantification of MPs was proposed very recently by Coimbra et al. (2005). The reference analysis is based on quantification of mannose, the main mannoprotein monosaccharide. It is more difficult to apply the methodology to AGPs and RG-II whose glycoside compositions are more complex (Vidal, Williams, Doco, Moutounet, & Pellerin, 2003).

This preliminary work was aimed at characterising the spectra of these various purified polysaccharides. Such spectral identification of each polysaccharide family (PRAGs, MPs, and RG-II) in wines has not been reported previously. We considered it important for future polysaccharide quantification by FTIR.

Table 1
Composition of the purified polysaccharides fractions

| Glycosyl residue[a] | RG-I1 | RG-I2 | RG-II2 | RG-II3 | AGP0c | AGP2 | AGP3 | AGP4 | MP0 | MP0a | MP0b | MP0c | MP1 | MP2 | MP3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MW (kDa)[b] | 44 | 52 | 10 | 5 | 48 | 105 | 192 | 177 | 351 | 337 | 62 | 51 | 301 | 311 | 527 |
| Arabinose[c] | 2.4 | 2.7 | 9.2 | 8.4 | 36.4 | 40.2 | 36.9 | 24.3 | 2.3 | 4.1 | 5.2 | tr | 4.5 | tr | 1 |
| Rhamnose | 26.6 | 30.0 | 14.2 | 15.5 | 1.4 | 3.9 | 9.2 | 14.1 | – | tr | tr | – | tr | – | tr |
| Fucose | 4.1 | 4.9 | 3.0 | 4.1 | – | – | – | tr | – | – | – | – | – | – | – |
| Xylose | 6.7 | 5.4 | – | – | tr | tr | – | 2.6 | – | – | – | – | – | – | – |
| Mannose | 0.9 | 1.0 | tr[f] | tr | 1.6 | 2.0 | 3.8 | 5.0 | 91.3 | 92.4 | 88.8 | 97.1 | 89.0 | 95.9 | 91.1 |
| Galactose | 4.8 | 5.6 | 6.7 | 5.3 | 51.4 | 44.4 | 36.8 | 28.8 | 3.3 | 2.5 | 2.9 | 1.2 | 1.8 | – | 2.4 |
| Glucose | 7.8 | 1.2 | – | – | 5.6 | 1.4 | tr | tr | 3.1 | – | 2.6 | 1.9 | 3.6 | 3.6 | 5.1 |
| Apiose | – | – | 4.9 | 5.8 | – | – | – | – | – | – | – | – | – | – | – |
| 2OMeXylose | – | – | 5.8 | 5.7 | – | – | – | – | – | – | – | – | – | – | – |
| 2OMeFucose | – | – | 4.8 | 5.0 | – | – | – | – | – | – | – | – | – | – | – |
| GalU | 45.4 | 46.0 | 33.6 | 33.6 | – | – | 5.6 | 9.6 | – | – | – | – | – | – | – |
| GlcU | 1.6 | 3.8 | 3.6 | 3.3 | 3.6 | 7.5 | 7.8 | 14.7 | – | – | – | – | – | – | – |
| Aceric acid | – | – | 8.7 | 8.5 | – | – | – | – | – | – | – | – | – | – | – |
| DHA | – | – | 2.5 | 2.5 | – | – | – | – | – | – | – | – | – | – | – |
| KDO | – | – | 2.8 | 3.0 | – | – | – | – | – | – | – | – | – | – | – |
| Proteins[d] | na[e] | na | na | na | 3.6 | 3.0 | 2.4 | 0.8 | na | 1.4 | 1.6 | 3.5 | 2.4 | 2.9 | 9.3 |
| Phosphorus[d] | na | na | na | na | na | na | na | na | 0.13 | na | na | na | 0.34 | 0.43 | na |

[a] From Vidal et al. (2003) except AGPs Proteins from Pellerin et al. (1995) and Phosphorus from Vernhet et al. (1996).
[b] Apparent MW.
[c] Ratio of anhydromoles.
[d] Percent of dry matter.
[e] na, not analysed.
[f] tr, trace; $0 < \text{value} < 1$.

## 2. Materials and methods

### 2.1. Purified polysaccharide extracts

The different purified polysaccharides used have been isolated and characterized since 1995 in our laboratory (Pellerin et al., 1996, 1995). Their chemical composition was described by Vidal et al. (2003) and is summarised in Table 1.

### 2.2. Spectral acquisition conditions

Spectral acquisition was performed on solid samples using an Avatar 360 spectrometer equipped with Omnic software and an ATR cell with a single reflectance germanium crystal (Nicolet, Madison, USA). Each recorded spectrum is the average of 60 repetitions from 950 to 1850 $cm^{-1}$ with a 2 $cm^{-1}$ spectral resolution. A micrometric screw applying constant pressure ensured good contact between the sample and the crystal. The background spectrum was acquired in air twice a day. A sample-less spectrum was recorded between two polysaccharide fractions to monitor the stability of the background.

Each spectrum was subjected to linear standardisation at absorbance values from 0 to 1 for the respective wave numbers of 1800 and 1040 $cm^{-1}$.

### 2.3. Data processing

The multivariate analysis were processed using PLS-Toolbox 3.0 software (Eigenvector Research, USA) in a Matlab environment (Mathworks, USA).

## 3. Results and discussion

### 3.1. Main absorbance peak in FTIR spectra of RG-Is, RG-IIs, AGPs and MPs

The three main families of wine polysaccharides are those with the largest quantities isolated from a red wine made from the variety 'Carignan': RG-IIs, AGPs and MPs (Pellerin & Cabanis, 1998; Vidal et al., 2003). RG-II is a pectic polysaccharide of small molecular size and a complex structure. The principal chain consists of seven to nine linked galacturonic acids at α-(1 → 4) with four different lateral chains consisting of residues of 2-*O*-methyl-fucopyranose, 2-*O*-methyl-xylopyranose, apiose, Kdo, Dha, aceric acid, galactose, rhamnose, arabinose, fucose, galacturonic and glucuronic acids (Pellerin et al., 1995; Vidal et al., 2000). The AGP family consists mainly of arabinose and galactose, but in wine, AGPs differ in their percentages of uronic acids, the degree of polymerisation and the spatial distribution of branching (Pellerin et al.,

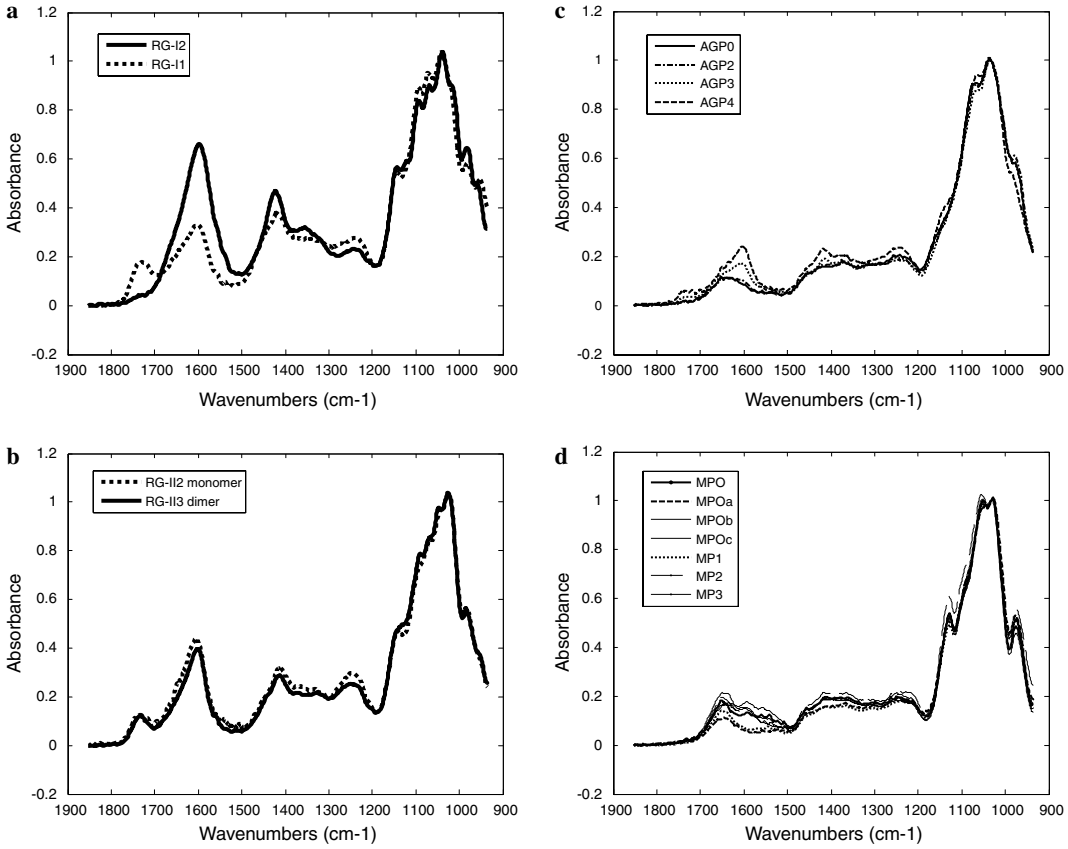


Fig. 1. Spectra of RG-Is (a), RG-II monomer and dimer (b), AGPs (c) and MPs (d), extracted from a red wine (Vidal et al., 2003).

1995; Vidal et al., 2003). As an example, the proportion of glucuronic and galacturonic acids ranges from 3.6% in AGP0 to 24.3% in AGP4 (Table 1) (Vidal et al., 2003). The MPs consist of 90% mannose and differ in their protein levels (1.4–9.3%) and by the presence of phosphoric acid (Vidal et al., 2003). RG-I is fairly abundant in grape berry walls (Vidal, Williams, O'Neill, & Pellerin, 2001). However, only small quantities of RG-I (<20 mg/l) are found in red wines but the FTIR spectrum of RG-I is interesting as its structure consists of repetition units of (→ 2)-α-L-Rha*p*-(1 → 4)-α-D-Gal*p*A-(1→) substituted on rhamnose by lateral arabinan and arabinogalactan chains.

The spectrum of each polysaccharide family is shown in Fig. 1a–d.

Maximum absorbance of all the polysaccharides are in the 950–1200 $cm^{-1}$ zone where the C—O—C and C—O—H link band positions are found (Kacurakova, Capek, Sasinkova, Wellner, & Ebringerova, 2000). The four polysaccharide families peaked at towards 1045 $cm^{-1}$. However, their profiles are quite different. The number of peak shoulders increases from AGPs to MPs, then RG-II and finally RG-I. There are just one small shoulder at 980 $cm^{-1}$ in the AGP spectra (Fig. 1c), two very distinct peaks at 1130 and 980 $cm^{-1}$ in the MP spectra (Fig. 1d), three peaks at 980, 1070 and 1145 $cm^{-1}$ in the RG-II spectra (Fig. 1b) and five peaks at 980, 1017, 1070, 1095 and 1145 $cm^{-1}$ in the RG-I spectra. The two MP peaks at 1130 and 980 $cm^{-1}$ are described by Kacurakova et al. (2000) and attributed to glycosidic links at α-(1 → 3). Wine polysaccharides, and especially mannoproteins (Saulnier, Mercereau, & Vezinhet, 1991; Waters, Wallace, Tate, & Williams, 1993), possess branches at α-(1 → 3) and the difference in spectral response intensity at 1130 and 980 $cm^{-1}$ might be related to the size of the lateral chains. Those of MPs branched at α-(1 → 3) are shorter at several monomers (Ballou, 1976) and would cause greater absorbance. The absence of peaks in the AGP spectra is more surprising. The core structure of AGPs consists of main β-D-galactopyranose chains linked at position 3 and strongly substituted at position 6 by other principal chains of β-D-galactopyranose linked in position 3 (Brillouet et al., 1990). We can put forward two possible explanations. Either the absorbance of the β-(1 → 3) galactan chains is masked as a result of the size of the lateral chains and appears to give a smaller spectral response at 1130 and 980 $cm^{-1}$ or, in contrast with α-(1 → 3), the β-(1 → 3) links do not give absorbance peaks.

The presence of many small absorbance peaks in the RG-I and RG-II spectra can be explained by the more complicated chemical structure. The RG-II core is a seven to eight galacturonic acid chain with four lateral chains from 2 to 10 residues (Vidal et al., 2001). The RG-I core is a ( → 2)-α-L-Rha*p*-(1 → 4)-α-D-Gal*p*A-(1→) main chain highly substituted with arabinose, galactose, xylans, arabinans, galactans, etc. RG-I displays great variability in the size, linkages and chemical composition of the lateral chains. RG-II always has the same chemical composition and the same structure but its 5 kDa monomer form is made up of at least 13 different monomers (Vidal et al., 2003). The monomer diversity in RG-Is and RG-IIs may account for the different absorbance peaks observed at 1017, 1070, 1095 and 1145 $cm^{-1}$ but not yet attributed.

From 1200 to 1800 $cm^{-1}$, the distinctly smaller absorbance of the oses means that the spectral signature of minor components of the polysaccharides—proteins and uronic acids—can be sought. Protein spectra are characterised by three bands of decreasing intensity: amide I towards 1650 $cm^{-1}$, amide II towards 1550 $cm^{-1}$ with N—H and C—N links, and amide III towards 1400 $cm^{-1}$(Bertrand & Dufour, 2000). MP spectra display an important peak at 1650 $cm^{-1}$, corresponding precisely to the amide I band. The MP peaks towards 1550 $cm^{-1}$ observed for MPO, MPOb, MPOc, MP2 and MP3 can then be attributed to the amide II peak.

Uronic acids are characterised by the carboxylic function which can lead to three absorbance peaks. The band towards 1750 $cm^{-1}$ is attributed to stretching vibration of C=O in the methyl-esterified carboxyl group or in COOH protonated carboxylic acid (Manrique & Lajolo, 2002). Two peaks towards 1620 and 1420 $cm^{-1}$ are attributed to the absorbance of the $COO^-$ deprotonated carboxylic function (Manrique & Lajolo, 2002; Marry et al., 2000; Monsoor, Kalapathy, & Proctor, 2001).

The two polysaccharide families RG-Is and RG-IIs are those richest in uronic acids (Vidal et al., 2003). They display the three very distinct absorbance peaks at 1735, 1600 and 1420 $cm^{-1}$ that therefore result from the presence of high uronic acids concentrations.

### 3.2. Spectrum variability in each of the four families of polysaccharides

Even if each family of polysaccharides has its own characteristic profile, differences within the polysaccharide fractions of the same family can be observed.

Between RG-I1 and RG-I2 (Fig. 1a) the differences are located in the 1200–1800 $cm^{-1}$ zone. RG-I1 displays higher absorbances than RG-I2 at 1620 and 1420 $cm^{-1}$ and lower absorbances at 1750 and 1240 $cm^{-1}$. The 1750 $cm^{-1}$ peak may be due either to the methyl esterified carboxylic group or to the protonated carboxylic acid. RG-I1 and RG-I2 were separated by anion-exchange chromatography (Vidal et al., 2003) and thus had different ionic charges whereas these two fractions contain much the same amounts of uronic acids: 47 and 49.8, respectively (Vidal et al., 2003). The RG-I 1750 $cm^{-1}$ peak can then be attributed to the methyl esterified carboxylic function and not to protonated carboxylic acid. This agrees well with the decrease of absorbance of the $COO^-$ function at 1620 and 1420 $cm^{-1}$ and with an increase of RG-I1 absorbance towards 1240 $cm^{-1}$ corresponding to a methyl-ester absorbance peak (Synytsya, Copikova, Matejka, & Machovic, 2003).

RG-II2 and RG-II3, the monomer and dimer forms (Fig. 1b) (Vidal et al., 2003), have a similar spectrum. The galacturonic acids of RG-IIs are partially methyl esterified (Pellerin et al., 1996; Puvanesarajah, Darvill, & Albersheim, 1991), with the degree of esterification depending on the prior treatment of the grape berry cell walls. This explains the absorbance peak at 1750 $cm^{-1}$.

The spectra of MPs differ with each other particularly between 1500 and 1700 $cm^{-1}$ . In this region, all the spectra have roughly the same shape with a peak at 1650 $cm^{-1}$ but there are differences in the absorbance levels. The upper and lower values are attributed to MP0a and MP3, respectively. As it corresponds to the amide II peak, the differences are explained by the proteic composition. However, if we rank the MP fractions (1) with their absorbance at 1550 $cm^{-1}$ and (2) with their total proteic composition (Table 1), some samples like MP0c are misclassified. There is probably another effect resulting from the nature of the proteins involved in the different MP fractions.

The main differences between the spectra of the different AGP fractions are encountered in the 1200–1800 $cm^{-1}$ region. The absorbances are lower for AGP0c and AGP2. They then increase with AGP3 and AGP4. The peak at 1640 $cm^{-1}$ with AGP0 and AGP4 shifts to 1600 $cm^{-1}$ with AGP3 and AGP4. All the AGP fractions contain hydroxyprolin-rich proteins (Pellerin & Cabanis, 1998); the mean is 3–4%. As AGP0c and AGP2 have low uronic acid concentrations, the 1640 $cm^{-1}$ peak corresponds to the amide I function. When the uronic acid concentrations with AGP3 and AGP4, the $COO^-$ corboxylic function also has an effect, explaining why the peak shifts from 1640 towards 1600 $cm^{-1}$.

### 3.3. Visualisation of spectral variability

Overall analysis of the FTIR spectra of the 15 purified polysaccharides was performed using PCA. Axis 1 represents 98.05% of the variability, confirming the high level of colinearity between these spectra. The differences between the 15 samples are more visible on axes 2 and 3 (Fig. 2) that together represent 1.66% of variability. Two clearly separate groups appear: (a) the MPs originating in yeast and (b) the AGP, RG-I, and RG-II families released from the grape berry cell walls. The individuals of the latter group form a continuum with an increasing uronic acid content from AGP0 to AGP-4/RG-II/RG-I. The loadings (Fig. 2b) give information on the first 3 principal components. The first loading represents an average polysaccharide spectrum. All the PS spectra are therefore very close one to the other with the differences between all of the PS fractions representing only 2% of the variability of the spectra. In the second loading, 3 peaks at 1730, 1600 and 1420 $cm^{-1}$ correspond to the different absorption peaks of the carboxylic function. This second set of principal components is helpful for separating the polysaccharide fractions according to their uronic acid concentrations.

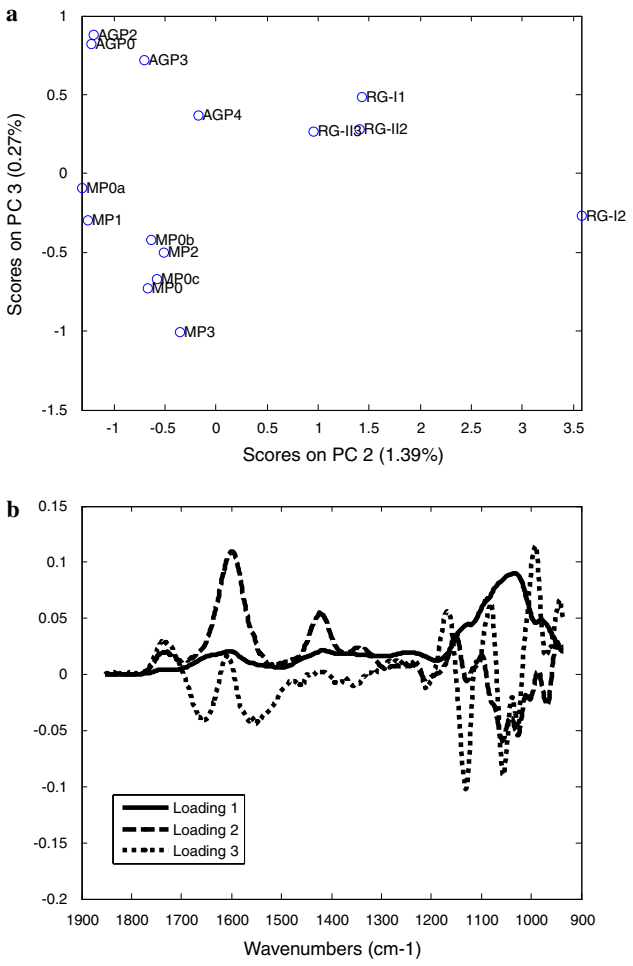


Fig. 2. (a) PCA on the spectra of the wine polysaccharides fractions. (b) First loadings of the principal components analysis.

The third loading displays negative coefficients at 1650 and 1550 $cm^{-1}$, corresponding to the amide I and amide II bands. This explains why MP fractions are well separated in the third principal components and also justifies the attribution of amide I and amide II functions to the peaks observed in the MP, MP0c and MP2 spectra. Explanation of the 950–1200 $cm^{-1}$ region of loadings 2 and 3 is more complicated as regards the chemical composition. The loadings generally peak at wave numbers that are between the maximum absorbance peaks of the polysaccharides.

## 4. Conclusion

This work presents for the first time the MIR spectra of the main polysaccharides in wines: Rhamnogalacturonans (RG-Is, RG-IIs), Polysaccharide rich in Arabinose and Galactose (AGPs) and Mannoproteins (MPs). The first three result from the degradation of the grape berry cell walls and the fourth is from yeast walls. The spectra show that each of the different polysaccharide families has a characteristic profile but that there is also non-negligible variability within each family. The presence of more or less

esterified uronic acids results in greater absorbance between 1200 and 1800 $cm^{-1}$.

Quantification of the main families of polysaccharides in wines by FTIR analysis will have to overcome the strong colinearity between the polysaccharide reference spectra and the intra-family spectral variability. Another problem is that wines contain low concentrations of polysaccharides, as mentioned above, and so direct quantification in wines is quite difficult with IRTF. A preliminary concentration-purification step is necessary. The quantification of wine polysaccharides from a wine extract is possible (Coimbra et al., 2005) but chemometric tools will be necessary to improve the accuracy and robustness of the models.

## References


Ballou, C. (1976). The structure and biosynthesis of mannan component of the yeast cell envelope. *Advanced Microbiology and Physiology, 14*, 93–158.

Belleville, M. P., Brillouet, J. M., Tarodo de la Fuente, B., & Moutounet, M. (1990). Polysaccharide effects on cross-flow microfiltration of two red wines with a microporous alumina membrane. *Journal of Food Science, 55*, 1598–1602.

Bertrand, D., & Dufour, E. (2000). *La spectroscopie infra-rouge et ses applications analytiques*. Technique & Documentation, Paris: Lavoisier.

Brillouet, J. M., Bosso, C., & Moutounet, M. (1990). Isolation, purification and characterization of an arabinogalactan from a red wine. *American Journal of Enology and Viticulture, 41*, 29–36.

Chalier, P., Angot, B., Delteil, D., Doco, T., & Gunata, Z. (2007). Interaction between aroma compounds and whole mannoprotein isolated from *Saccharomyces cerevisiae* strains. *Food Chemistry, 100*, 22–30.

Coimbra, A. C., Barros, A. S., Coelho, E., Gonçalves, F., Rocha, M. S., & Delgadillo, I. (2005). Quantification of polymeric mannose in wine extracts by FT-IR spectroscopy and OSC-PLS1 regression. *Carbohydrate Polymers, 61*, 434–440.

Doco, T., & Brillouet, J. M. (1993). Isolation and characterization of a rhamnogalacturonan II from red wine. *Carbohydrate Research, 243*, 333–343.

Doco, T., Quellec, N., & Moutounet, M. (1999). Polysaccharide patterns during the aging of Carignan noir red wines. *American Journal of Enology and Viticulture, 50*, 25–32.

Dubernet, M., & Dubernet, M. (2000). Utilisation de l'analyse infrarouge à transformée de Fourier pour l'analyse œnologique de routine. *Revue Française d'œnologie, 181*, 10–13.

Fayolle, P., Picque, D., Perret, B., Latrille, E., & Corrieu, G. (1996). Determination of major compounds of alcoholic fermentation by middle infrared spectroscopy : Study of temperature effects and calibration methods. *Applied spectroscopy, 50*(10), 1325–1330.

Gerbaud, V., Gabas, N., Blouin, J., Pellerin, P., & Moutounet, M. (1997). Influence of wine polysaccharides and polyphénols on the cristallization of potassium hydrogen tartrate. *Journal International des Sciences de la Vigne et du Vin, 31*(2), 65–83.

Gerbaud, V., Gabas, N., Laguerie, C., Blouin, J., Vidal, S., Moutounet, M., et al. (1996). Effect of wine polysaccharides on the nucleation of potassium hydrogen tartrate in model solutions. *Transaction of Institution of Chemical Engineers, 74*, 782–790.

Kacurakova, M., Capek, P., Sasinkova, V., Wellner, N., & Ebringerova, A. (2000). FT-IR study of plant cell wall model compounds: Pectic polysaccharides and hemicelluloses. *Carbohydrate Polymers, 43*, 195–203.

Kupina, S. A., & Shrikhande, A. J. (2003). Evaluation of a fourier transform infrared instrument for rapid quality-control wine analyses. *American Journal of Enology and Viticulture, 54*(2), 131–134.

Llaubères, R. M., Dubourdieu, D., & Villetaz, J. C. (1987). Exocellular polysaccharides from Saccharomyces in wines. *Journal of the Sciences of Food and Agriculture, 41*, 267–286.

Manrique, G. D., & Lajolo, F. M. (2002). FT-IR spectroscopy as a tool for measuring degree of methyl esterification in pectins isolated from ripening papaya fruit. *Postharvest Biology and Technology, 25*, 99–107.

Marry, M., McCann, M., Kolpak, F., White, A. R., Stacey, N., & Roberts, K. (2000). Extraction of pectic polysaccharides from sugar-beet cell walls. *Journal of the Sciences of Food and Agriculture, 80*, 17–18.

Moine, V. & Dubourdieu, D. (1996). Mise au point d'une préparation industrielle de la levure, améliorant la stabilité protéique et inhibant les précipitations tartriques. In Lonvaud-Funel, A. *Oenologie* (Vol. 95, pp. 385–390). Paris: Lavoisier.

Monsoor, M. A., Kalapathy, U., & Proctor, A. (2001). Determination of polygalacturonic acid content in pectin extracts by diffuse reflectance Fourier transform infrared spectroscopy. *Food Chemistry, 74*, 233–238.

O'Neill, MA., Warrenfeltz, D., Kates, K., Pellerin, P., Doco, T., Darvill, A. G., et al. (1996). Rhamnogalacturonan II, a pectic polysaccharide in the walls of growing plant, forms a dimer that is covalently cross-linked by borate ester. In vitro conditions for the formation and hydrolysis of the dimer. *Journal of Biological Chemistry, 271*, 22923–22930.

Patz, C. D., David, A., Thente, K., Kurbel, P., & Dietrich, H. (1999). Wine analysis with FTIR spectrometry. *Viticultural and Enological Sciences, 54*, 80–87.

Pellerin, P., & Cabanis, J. C. (1998). Les Glucides. In C. Flanzy, *Elements d'œnologie. Fondements scientifiques et techniques* (pp. 40–93). Technique et Documentation. Paris : Lavoisier.

Pellerin, P., Doco, T., Vidal, S., Williams, P., Brillouet, J. M., & O'Neill, M. A. (1996). Structural characterization of red wine rhamnogalacturonan II. *Carbohydrate Research, 290*, 183–197.

Pellerin, P., O'Neill, M. A., Pierre, C., Cabanis, M. T., Darvill, A., Albersheim, P., et al. (1997). Lead present in wines is bound to the dimers of rhamnogalacturonan II, a pectic polysaccharide from the grape berry cell walls. *Journal International des Sciences de la Vigne et du Vin*, 33–41.

Pellerin, P., Vidal, S., Williams, P., & Brillouet, J. M. (1995). Characterization of five type II arabinogalactan-protein fractions from red wine of increasing uronic acid content. *Carbohydrate Research, 277*, 135–143.

Puvanesarajah, V., Darvill, A. G., & Albersheim, P. (1991). Structural characterization of two oligosaccharide fragments formed by the selective cleavage of Rhamnogalacturonan II: evidence for the anomeric configuration and attachment sites of apiose and 3-deoxy-2 heptolosaric acid. *Carbohydrate Research, 218*, 211–222.

Riou, V., Vernhet, A., Doco, T., & Moutounet, M. (2002). Aggregation of grape seed tannins in model wine-effect of wine polysaccharides. *Food Hydrocolloid, 16*, 17–23.

Saulnier, L., Mercereau, T., & Vezinhet, F. (1991). Mannoproteins from flocculating and non-flocculating *Saccharomyces cerevisiae* yeasts. *Journal of the Sciences of Food and Agriculture, 54*, 275–286.

Schneider, R., Charrier, F., Moutounet, M., & Baumes, R. (2004). Rapid analysis of grape aroma glycoconjugates using Fourier-transform infrared spectroscopy and chemometrics techniques. *Analytica Chimica Acta, 513*, 91–96.

Semichon, L. (1927). Les pectines des raisins et le moelleux des vins. *Chimie et Industrie, 17*, 25–32.

Synytsya, A., Copikova, J., Matejka, P., & Machovic, V. (2003). Fourier-transform Raman and infrared spectroscopy of pectins. *Carbohydrate Polymers, 54*, 97–106.

Vernhet, A., Pellerin, P., Belleville, M. P., Planque, J., & Moutounet, M. (1999). Relative impact of major wine polysaccharides on the performances of an organic microfiltration membrane. *American Journal of Enology and Viticulture, 50*, 51–56.

Vernhet, A., Pellerin, P., Prieur, C., Osmianski, I., & Moutounet, M. (1996). Charge properties of some grape and wine polysaccharidic and polyphenolic fractions. *American Journal of Enology and Viticulture, 47*, 25–30.

Vidal, S., Doco, T., Moutounet, M., & Pellerin, P. (2000). Soluble polysaccharide content at initial time of experimental must preparation. *American Journal of Enology and Viticulture, 51*, 115–121.

Vidal, S., Williams, P., Doco, T., Moutounet, M., & Pellerin, P. (2003). The polysaccharides of red wine: Total fractionation and characterisation. *Carbohydrate Polymers, 54*, 439–447.

Vidal, S., Williams, P., O'Neill, M. A., & Pellerin, P. (2001). Polysaccharides from grape berry cell walls. Part I: Tissue distribution and structural characterization of the pectic polysaccharides. *Carbohydrate Polymers, 45*, 315–323.

Waters, E. J., Pellerin, P., & Brillouet, J. M. (1994). A Saccharomyces mannoprotein that protects wine from protein haze. *Carbohydrate Polymers, 23*, 185–191.

Waters, E. J., Wallace, W., Tate, M. E., & Williams, P. J. (1993). Isolation and partial characterization of a natural haze protective factor from wine. *Journal of Agricultural and Food Chemistry, 41*, 724–730.