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Solid State Characterization of Croatian Wine Grape Pomace by NMR and ATR-FTIR

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Abstract: Grape pomace (GP), the solid residues remained after production of the continental and coastal Croatian red wines, has been studied by solid-state NMR and ATR-FTIR methods. After collection, drying and milling, GP samples have been analysed by IR spectroscopy and characteristic vibrational bands have been assigned. The observed differences in some functional group vibrations have been detected for continental and coastal GPs as well as for different vintages. ^{13}C cross-polarization magic angle spinning (CP MAS) NMR experiments provided further information on chemical composition of GPs and percentages of different compounds present in the samples such as polysaccharides and phenolic compounds. ^{31}P MAS spectra gave valuable quantitative information on the phosphorus content. The GPs from the continental varieties contain much larger portion of phosphorus compared to coastal ones, which is important for their potential use as an attractive raw material and value-added compounds for industrial applications.

Keywords: grape pomace, solid-state characterization, ssNMR, ATR-IR.

INTRODUCTION

WINE production is one of the most important industries on the global level, generating great economic value.[1] According to Agriculture and rural development of European Commission and the Food and Agriculture Organization, the European Union is the world-leading producer of wine with Italy, France and Spain as main producers.[1,2] Consequently, wine production generates 20 million tons of biological residues annually.[3]

Grape pomace (GP) is the main solid biological residue obtained after grape crushing and represents around 20–25 % of the total processed mass.[4] It contains leftover pulp, seeds, skins and optionally stems.

In Croatia, wine production has a long and rich tradition, and thanks to the diversity of climate and soil conditions, Croatia has a large number of autochthonous varieties.[5] Approximately 1 kg of pomace is produced for every 6 litres of wine, and it is estimated that around 40,600 tons of pomace are produced in Croatia annually.[6]

The chemical composition of GP is influenced by many factors, such as collection method, grape variety, year of harvest, climatic conditions, geographical origin, ampelotechnical measures applied during cultivation and the conditions during GP storage.[7,8] In Croatia, GP is most commonly used for the production of "Komovica" brandy.

GP is complex lignocellulosic substrate rich in valuable ingredients, including polysaccharides, proteins, vitamins, minerals, fibres, fatty acids and natural antioxidants, especially phenolic compounds. About 70 % of phenolic compounds remain in the GP after wine production. Phenolic compounds belonging to the flavonoids, such as flavanols, flavonols, anthocyanins, isoflavones and phenolic acids, make GP a very valuable material that benefits human health due to its antioxidant, anti-inflammatory, anti-cancer, cytotoxic and anti-microbial properties.[9] This residue therefore has a great potential to be utilized for various purposes, such as use in the production of citric acid, in the formulation of animal feed and human food, and in the pharmaceutical and cosmetic industry.[10] In addition, GP is a promising renewable resource for the production of high-quality products, including biofuels and various value-added products.[11] A detailed understanding of the composition and properties of GP is crucial for its correct use. Furthermore, due to the complex chemical composition of the grape pomace, pre-treatment is a critical step to reduce its recalcitrance into a less recalcitrant form (less complex structural form). During the last decades various pretreatment methods were developed, including ball milling (BM), hydrothermal (HT), dilute acid (DA), alkaline (AP), and combined wet alkaline mechanical (ABM) pretreatment.[12] Significant efforts are dedicated also to biological methods, particularly the implementation of fungi.[13–15]

In winery, the solid residual fractions are usually disposed of directly in the fields without any pre-treatment, contributing to the environmental pollution due to the release of many different volatile organic compounds.[16] Due to economic reasons and environmental concerns many researchers are focused on finding new ways of GP handling, such as use in encapsulation techniques[4] and production of food enriched by fibres and polyphenols.[7] Due to the heterogeneous composition of GP, it is essential to know the exact chemical composition, which requires a fast analytical method.

NMR can provide valuable data on the molecular architecture and composition of GP. Compared to other classical or instrumental methods NMR is advantageous due to simple and non-invasive sample preparation. Solution and solid-state NMR spectroscopy was proven useful to study different wine samples for metabolomic profiling and tracing the geographical origin and authenticity of wine.[17–20] Another advantage of solid-state NMR spectroscopy is the fact that no physical separation of the components prior to analysis is needed and no internal standard is necessary for quantitative analysis. Since GP contains a considerable amount of polysaccharides and the extraction, characterization and utilisation of polysaccharides from red GP has not yet been clarified, this area is attracting the attention of many NMR research groups.[21] The typical peak distributions for polysaccharides originated from lignocellulosic samples range between 3.0 and 5.5 ppm for protons and 55 to 110 ppm for carbons. GPs consist of 17–25 % lignin, making them an attractive raw material and value-added compounds for various industrial applications.[22]

In addition to NMR, FTIR spectroscopy has been also applied for the rapid monitoring and identification of functional groups of GP samples, such as characterisation of tannin extracts, phenolic-rich extracts and hydrocolloid biopolymers.[23–27]

In this work, we used solid-state NMR techniques (^{1}H, ^{13}C and ^{31}P) and ATR-IR to analyse chemical composition of five GP samples obtained from different Croatian red grape varieties of the continental (Erdut) and coastal regions (Pelješac) in their native state without solubilisation. We were keen to investigate the potential of these techniques for solid-state characterization of GP.

EXPERIMENTAL

Sample Collection and Preparation

Different varieties of GP consisting of seeds, pomace and skins, were used in this study. Specifically, Erdut winery (Erdut, eastern Croatia) supplied Cabernet Franc (harvest 2020), Cabernet Sauvignon (harvest 2017 and 2020), and Merlot (harvest 2020), while Plavac Mali (harvest 2024) was obtained from Pelješac region. After collection, the GP samples were dried in a laboratory drying oven (Venticell 111, MMM Group, Germany) for 24 h at 50 °C with an adjusted aeration of 60 %. Prior to analysis, the samples of pomace were milled using an ultracentrifugal mill (Retsch ZM 200, Haan, Germany) to achieve a particle size of ≤ 1 mm and stored at ambient temperature.

ATR-FTIR Measurements

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermo Fisher Scientific Nicolet iS50 FTIR Spectrometer equipped with HeNe laser and ATR sampling accessory. The number of scans accumulated for each spectrum was 8 at a spectral resolution of 4 cm^{-1} in the range 4000–400 cm^{-1}.

NMR Measurements

4 mm NMR rotors were filled with dried and ground GP samples. NMR spectra in solid state were recorded on a Bruker Avance NEO 400 spectrometer equipped with a broad band magic angle spinning (MAS) probe. The samples were spun at the magic angle in 4 mm rotors at 15 kHz. ^{1}H MAS experiments were performed with 10 scans, 2.5 µs excitation pulse length, 3 s recycle delay and 0.40 s acquisition time. ^{13}C cross-polarization (CP) MAS spectra were recorded with 2000 scans, 3.5 s recycle delay and 40 ms acquisition time using a pulse sequence with high power decoupling during acquisition. Variable amplitude CP ramped from 70 % to a maximum of 100 kHz during the contact time of 2 ms. The SPINAL-64 scheme was used for proton decoupling during the acquisition period. Both

^{1}H MAS and ^{13}C CP MAS spectra were externally referenced to glycine. Quantitative ^{31}P MAS spectra were acquired with 1024 scans, 60 s recycle delay and 14 ms acquisition time using an hpdec sequence and SPINAL-64 proton decoupling. The external reference for ^{31}P MAS spectra was ammonium orthophosphate.

RESULTS AND DISCUSSION

NMR Spectroscopy

^{13}C CP MAS Spectral Analysis

^{13}C CP MAS NMR spectra of the Croatian continental and coastal red wine GP samples are displayed in Figure 1. Chemical composition of the investigated pomace samples has been determined by integrating specific spectral regions of ^{13}C CP MAS NMR spectra. As can be seen from the Table 1, the obtained values differ for all five pomaces. Furthermore, different values have been determined even within the same variety (Cabernet Sauvignon), but different harvest years (2017 and 2020). In general, most of the chemical groups in polysaccharides are found in the spectral range between 58–90 ppm. GP samples contain more than 43 % polysaccharide carbons, with GP residue of coastal Plavac Mali having a slightly lower percentage compared to those from the continental Erdut region due to varietal difference in grape cell wall composition or prolonged maceration of PM pomace which could increase the extraction of water-soluble and alcohol-soluble compounds *e.g.* polysaccharides. The relative percentage of carbonyl compounds is the highest in Cabernet Franc 2020, and the lowest for Merlot 2020, although the differences are relatively small. Furthermore, the results displayed in Table 1, indicate that the content of aliphatics observed in the region 0–50 ppm[28] is the highest in Cabernet Franc 2020, while aromatics are the most abundant in the Plavac Mali 2024 residue which can be attributed to the specific biochemical composition and warm climate growing conditions. The spectral range between 90 and 110 ppm belongs to the C–O–C groups of all three lignocellulosic biomass polymers *e.g.* lignin, hemicellulose and cellulose, which are valuable renewable resources. Results displayed in Table 1 show that the portion of C–O–C groups is similar in all GP samples being a little larger in Plavac Mali GP. For a full quantification of the components additional methods should be used such as multiple CP MAS for example.[29]

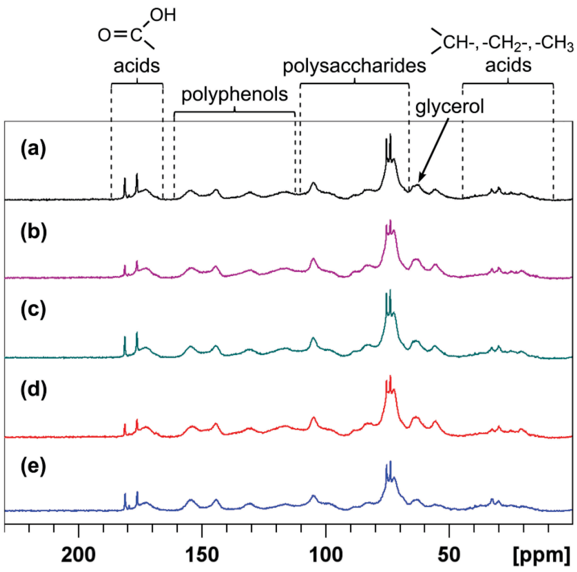

Figure 1. ^{13}C CP MAS NMR spectra of the GP samples: (a) Cabernet Franc 2020, (b) Cabernet Sauvignon 2017, (c) Cabernet Sauvignon 2020, (d) Merlot 2020 and (e) Plavac Mali 2024.

Table 1. The portions of specific functional groups determined from ^{13}C CP MAS spectra

Sample	aliphatic-C (0–50 ppm) / %	OCH_3 (50–58 ppm) / %	Polysaccharides (58–90 ppm) / %	O–C–O (90–110 ppm) / %	Polyphenols (110–140 ppm) / %	aromatic-C (145–165 ppm) / %	COO (165–185 ppm) / %
Cabernet Franc 2020	12.1	4.4	44.0	11.0	11.5	8.7	8.3
Cabernet Sauvignon 2017	9.7	4.9	44.9	10.7	13.2	9.4	6.9
Cabernet Sauvignon 2020	8.3	4.2	46.9	11.7	12.7	9.3	6.9
Merlot 2020	7.9	5.2	45.9	10.9	14.6	9.7	5.8
Plavac Mali 2024	11.7	3.2	43.9	13.0	10.7	10.6	6.9

Experimental error was less than ±0.5%

^{31}P and ^{1}H MAS Spectral Analyses

Phosphorus is one of the most important essential macronutrients for plants and plays a key role in regulating physiological and biochemical responses in plants. It is present in inorganic and organic forms.

Inorganic phosphorus is present in the form of orthophosphates, pyrophosphates and polyphosphates while organic phosphorus can usually be found in the form of phosphate monoesters and diesters, α- and β-glycerophosphates and organic polyphosphates. Since it plays a vital role in biochemical processes of living organisms and it is also used in many industrial applications, it is crucial to increase phosphorus production from bio-resources. Hence, it is of importance to determine the total amount of phosphorus in GP biomass by using direct, fast and non-invasive methods such as ssNMR.

Phosphorus solid-state NMR spectra of GP samples are displayed in Figure 2. It is clearly seen that the intensity of phosphorus in continental GP samples is much larger than that in the coastal Plavac Mali 2024 GP residue which make continental wine GPs a much better bioresource of phosphorus for its further exploitation. Coastal Dalmatian soils, like those present on Pelješac, are often karstic, rocky, and less fertile, with lower bioavailable phosphorus in the vineyard soil compared to the loamy, mineral-rich soils of continental regions (like Erdut). ^{31}P MAS NMR spectra directly reflect this difference.

We have also recorded ^{1}H MAS spectra of GP samples and the typical spectrum is displayed in Figure 3. Resonances appeared relatively narrow which is not common for proton solid-state NMR spectra.[30] This must be due to certain molecular mobility of the measured species, as is the case for fatty acid lipid chains. In fact, all GP samples contain significant amount of lipids and the lipid mobile chains dominate the ^{1}H MAS NMR spectra.

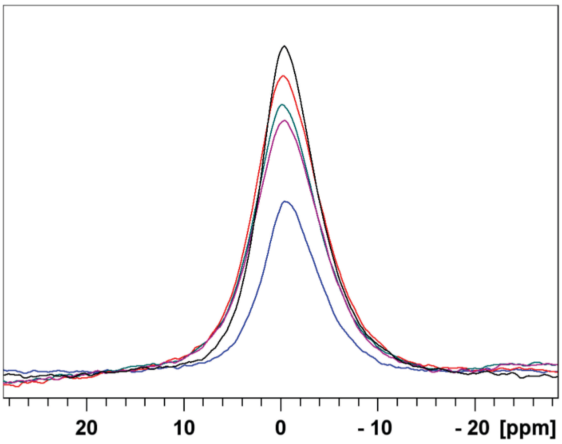

Figure 2. ^{31}P MAS NMR spectra of the GP samples. From top to bottom: Cabernet Franc 2020, Merlot 2020, Cabernet Sauvignon 2020, Cabernet Sauvignon 2017, Plavac Mali 2024.

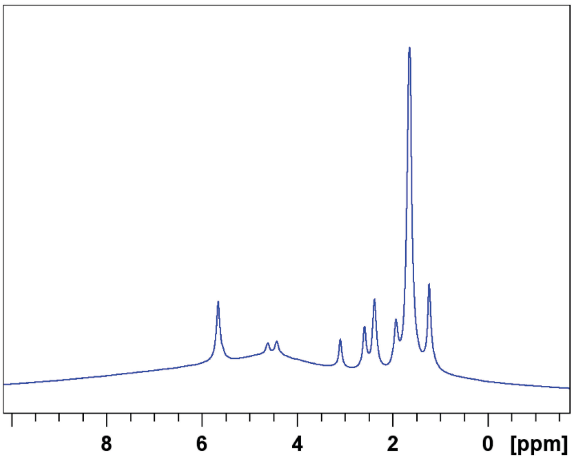

Figure 3. Representative ^{1}H MAS spectrum of Cabernet Franc 2020.

The resonances observed in ^{13}C CP MAS spectra around 30 ppm (Figure 1) corroborate the presence of lipids. Those signals were detected with lower intensity in the ^{13}C CP MAS NMR spectra because the cross-polarization efficiency depends on the ^{1}H-^{13}C dipolar coupling and thus CP spectra are dominated by signals of the rigid structures such as those in carbohydrates and the signals associated with mobile components should appear with reduced intensity. Hence, ^{1}H MAS spectra of GP samples are not as informative as ^{13}C and ^{31}P.

ATR-IR Spectroscopy

A typical IR spectrum of a continental red wine GP with characteristic vibrational bands is given in the Figure 4. IR spectra of other GP samples are given in the Supplementary material. Assignments of characteristic vibrational bands of GPs are displayed in the Table 2.

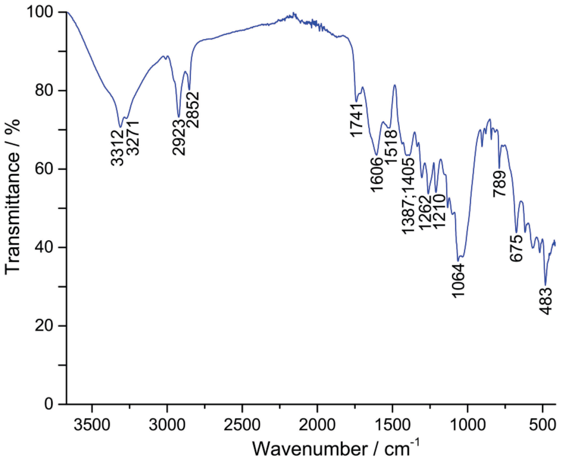

Figure 4. ATR-IR spectrum of Cabernet Franc 2020.

Table 2. Characteristic vibrational frequencies of the grape pomace samples

$\tilde{\nu}$ / cm^{-1}					Vibrational mode
Cabernet Franc 2020	Cabernet Sauvignon 2017	Cabernet Sauvignon 2020	Merlot 2020	Plavac Mali 2024	
3312	3312	3310	3309	3309	ν(O–H)
3271	3271	3271	3271	3268	ν(N–H)
2852; 2923	2853; 2922	2852; 2921	2852; 2923	2849; 2919	ν(C–H)
1741	1743	1742	1743	1712	ν(C=O)
1518; 1606	1519; 1610	1519; 1607	1518; 1608	1530; 1602	$\nu(\mathrm{C{=}C})_{\mathrm{ring}}$
1405	1409	1406	1407	–	$\nu(\mathrm{COO^{-}})$
1387	1379	–	1381	1386	$\delta(\mathrm{O{-}H})_{\mathrm{i.p.,\ phenol}}$
1210; 1262	1212; 1262	1211; 1262	1214; 1262	1208; 1260	ν(C–O)
1064	1030	1066	1063	1064	$\nu(\mathrm{C{-}O})_{\mathrm{gylcosylated\ phenol}}$
675; 789	675; 782	675; 790	677; 789	673; 789	$\gamma(\mathrm{C{-}H})_{\mathrm{o.o.p.,aromatic}}$
483	483	480	484	480	ν(S–S)

Abbreviations: i. p., in plane; o. o. p., out of plane

ATR-IR spectrum of Cabernet Franc 2020 shows a characteristic peak at 1741 cm^{-1} (Figure 4) belonging to the stretching vibration of the carbonyl C=O group reflecting the presence of tannins in the sample.[31,32] The position of this band does not change much in the GPs extracted from the continental varieties. On the other hand, the corresponding C=O stretching mode in GP extracted from the coastal Plavac Mali 2024 has shifted to a lower value of 1712 cm^{-1} reflecting structural change in tannins as compared to the continental sorts. Vibrational bands observed at 1606 cm^{-1} and 1518 cm^{-1} correspond to the stretching vibrations of the fragment C=C–C typical for aromatic systems. The latter band has been observed at somewhat higher value of 1530 cm^{-1} in Plavac Mali GP. The vibrational peak at 1387 cm^{-1} has been assigned to the bending vibration of the O–H group characteristic of phenols. The corresponding bands in other GPs varies to some smaller extent probably due to different phenolic compounds remained in the samples. Peaks at 1262 and 1210 cm^{-1} are due to the C–O stretching vibrational mode in esters. The peak at 1064 cm^{-1} has been assigned to the –COH group vibration of sugars in glycosylated phenols. Only in the case of Cabernet Sauvignon 2017 that band has been found at lower value of 1030 cm^{-1} indicating structural differences compared to other residues stemming from different vintages.

CONCLUSION

It has been demonstrated that NMR and ATR-IR are effective and non-destructive methods for characterization of Croatian red grape pomace in its native solid state providing valuable structural and quantitative information. Significant compositional differences were observed among GPs from continental and coastal regions, as well as between different harvest years of the same variety. Thus, GPs derived from continental varieties exhibited a higher phosphorus content, which makes it a promising phosphorus-rich bioresource. Our ongoing investigation is focused on environmental, varietal and vinification influence on these complex lignocellulosic substrates for their potential industrial applications.

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Supplementary Information. Supporting information to the paper is attached to the electronic version of the article at: https://doi.org/10.5562/cca4176.

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