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Data Descriptor

^{13}C NMR Dataset Qualitative Analysis of Grecian Wines

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Abstract: The development of analytical techniques for characterizing food samples, especially for the wine industry, is a main topic of research. Regarding the classification of wines based on their geographical origin, nuclear magnetic resonance (NMR) spectroscopy represents a fast and effective tool for determining chemical fingerprints. Herein, a ^{13}C NMR dataset, which was acquired for classification of Grecian wines through multivariate statistics, is reported and described. Thus, the main qualitative differences between grapes of the same geographical origin, observable by the visual analysis of the ^{13}C NMR data, are discussed.

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Keywords: wine; ^{13}C NMR; nuclear magnetic resonance; grape variety

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1. Summary

The development of new analytical techniques combined with statistics for possible applications in food chemistry and, in particular, in food classification and quality assessment is a topic of interest for many studies [1–5]. The possibility to employ, for such purposes, the raw data extracted from ^{13}C nuclear magnetic resonance (NMR) analysis for the geographical classification of Grecian wines has been recently explored [6]. In that case, selected portions of ^{13}C NMR spectra were extracted by a binning procedure, and the resulting integrals (independently from their physical meaning) were statistically treated. Herein, the original dataset, only partially published in the original manuscript, is reported and qualitatively described. The ^{13}C NMR spectra were grouped by a known geographical origin, and a qualitative discussion about the differences among different wines from the same region is provided. The samples were analyzed in pure form as collected from the original bottles. Additional details are given in the Methods section.

2. Data Description

The ^{13}C NMR analysis of 28 Grecian wine samples is herein described. Samples of different geographical origin and arising from different grapes and processes were considered (Table 1). The samples were grouped by geographical origin, and seven groups were generated: Crete, Samos Island, Ileia, Ioannina, Meteora, Korinthos, and Macedonia. The ^{13}C NMR spectra of each group are described in a dedicated section.

Table 1. The wine samples considered in the study.

ID	Year	Type	Origin	Variety
1	2017	Dry white wine—PDO	Zitsa, Ioannina	Debina
2	2017	Dry white wine—PGI	Crete	Malvasia di Candia Aromatica–Chardonnay
3	2016	Dry red wine—PGI	Crete	Syrah–Mandilari
4	2017	Dry rosé wine—PGI	Crete	Syrah–Mandilari
5	2017	Dry red wine—PGI	Crete	Syrah
6	2017	Dry white wine—PGI	Crete	Vidiano
7	2017	Dry white wine—PDO	Samos Island	Muscat
8	2017	Dry white wine	Samos Island	Muscat
9	2018	Semi-dry rosé wine	Samos Island	Samos red grapes
10	2011	Nectar, white wine naturally sweet—PDO	Samos Island	Muscat
11	2016	Dry red wine—PGI	Letrinoi, Ileia	Refosco
12	2015	Dry red wine—PGI	Letrinoi, Ileia	Daphne Nera–Mavrodafni
13	2016	Dry red wine—PGI	Ileia	Augoustiatis
14	2017	Dry white wine	Ileia	Albariño
15	2017	Demi-sec white wine	Zitsa, Ioannina	Debina
16	2016	Dry red wine—PGI	Meteora	Limniona
17	2017	Dry white wine—PGI	Meteora	Assyrtiko
18	2018	Dry white wine—PGI	Meteora	Malagouzia
19	2018	Dry white wine—PGI	Macedonia	Malagouzia
20	2016	Dry red wine—PGI	Zitsa, Ioannina	Vlahiko
21	2017	Dry rosé wine—PGI	Korinthos	Agiorgitiko
22	2017	Semi-sweet red wine—PGI	Korinthos	Agiorgitiko
23	2015	Dry red wine	Korinthos	Syrah/Merlot/Cabernet
24	2015	Dry red wine—PGI	Naoussa, Macedonia	Syrah–Xinomavro
25	2015	Dry red wine—PGI	Naoussa, Macedonia	Syrah
26	2015	Dry red wine—Table wine	Naoussa, Macedonia	Xinomavro–Mavroudi–Sefka
27	2016	Dry red wine—PDO	Naoussa, Macedonia	Xinomavro
28	2015	Dry red wine—PGI	Macedonia	Merlot–Xinomavro

PDO: protected designation of origin, PGI: protected geographical indication.

2.1. Crete Samples

The Crete group contains two white (Malvasia di Candia Aromatica–Chardonnay and Vidiano), two red (Syrah and Syrah–Mandilari), and one rosé wine (Syrah–Mandilari). The corresponding ^{13}C NMR spectra are reported in Figure 1.

From the ^{13}C NMR spectra reported in Figure 1, it is possible to notice that the pattern of signals associated with the Crete wines is similar for all the samples considered. As the five wines analyzed are quite different in terms of grapes, procedure, and year of preparation, more differences within the corresponding spectra were expected. This fact suggests that the common geography of these grapes strongly influences their chemical composition, leading to only small differences related to grape and production characteristics. The portions of the spectra most representative for these samples are the aliphatic part (10–40 ppm), as well as the part associated with carbon atoms near multiple bonds or to heteroatoms (40–80 ppm). Looking at the small differences, up to 50 ppm, only the dry rosé protected geographical indication (PGI) Syrah–Mandilari shows a different pattern of signals between 40 and 50 ppm. Looking at lower fields, dry red wine PGI Syrah–Mandilari and dry red wine Syrah reveal a small pattern between 90 and 105 ppm. Small signals just outside the background in the area of the quaternary carbons, around 180 ppm, can be noticed for all the samples.

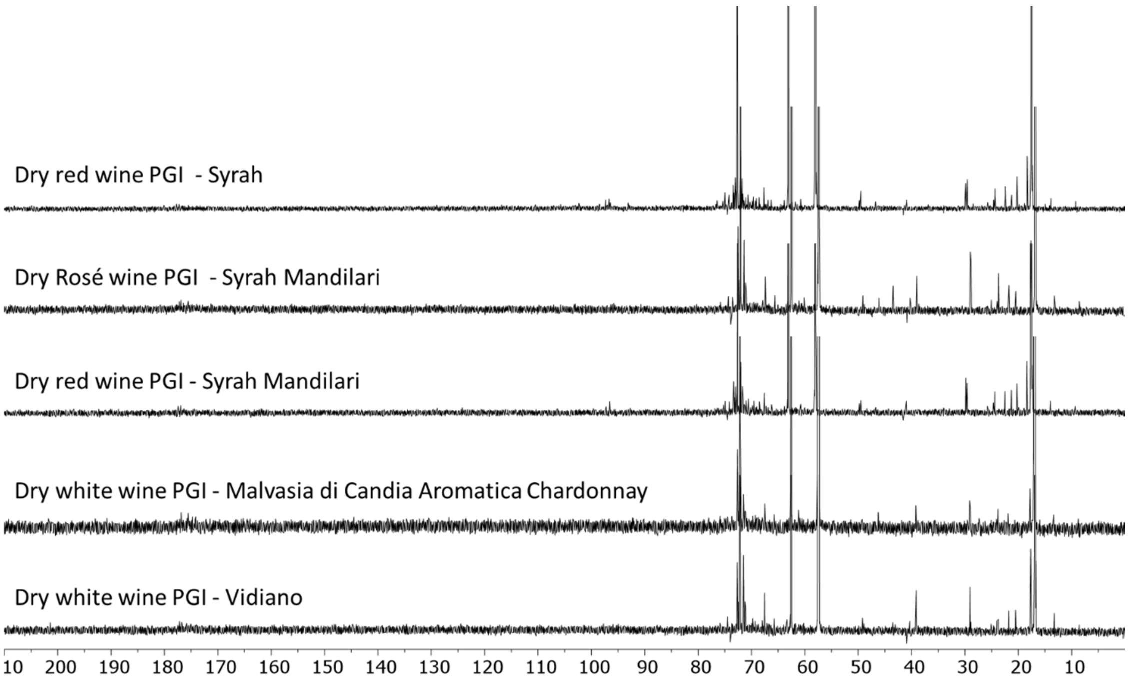

Figure 1. ^{13}C nuclear magnetic resonance (NMR) spectra of Crete wines.

2.2. Samos Island Samples

From Samos Island, four wines (three white and one rosé) were considered (Figure 2).

The three Muscat wines from Samos Island present a very similar pattern in their ^{13}C NMR spectra. The dry white DPO wine seems to contain fewer minor compounds with respect to the other two wines made by the same grape. Apart from the major pattern, the windows between 20 and 55 ppm, as well as from 110 to 210 ppm, are very clean. The spectrum of the semi-dry rosé wine shows a very similar pattern to the Muscat wines, suggesting (at a qualitative level) that the common geography determines the composition observable at ^{13}C NMR more than the specific type of grape.

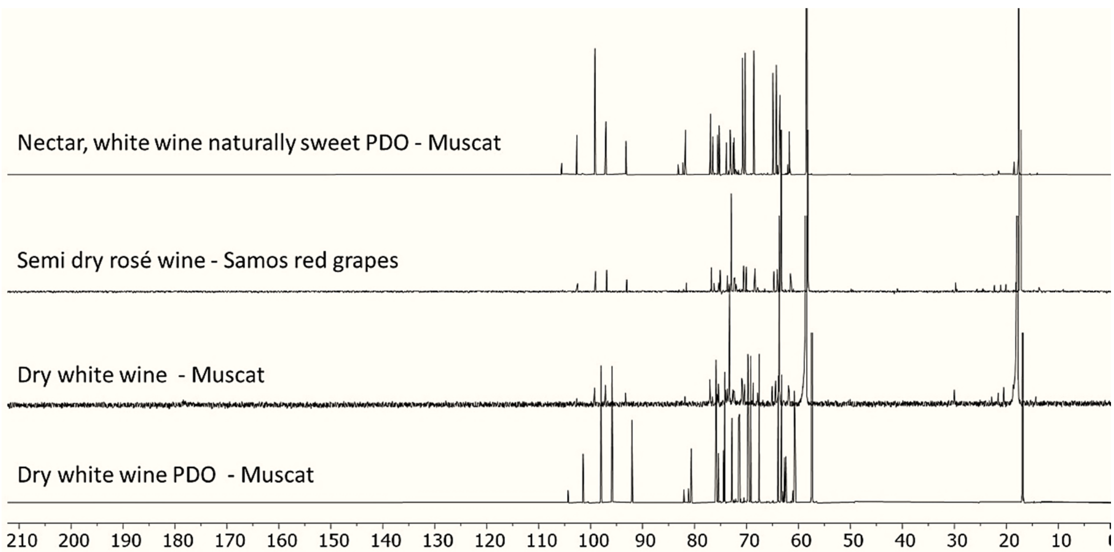

Figure 2. ^{13}C NMR spectra of Samos Island wines.

2.3. Ileia Samples

A total of four wines arising from Ileia were analyzed: one white (Albariño) and three red (Augoustiatis, Daphne Nera–Mavrodafni, and Refosco) (Figure 3).

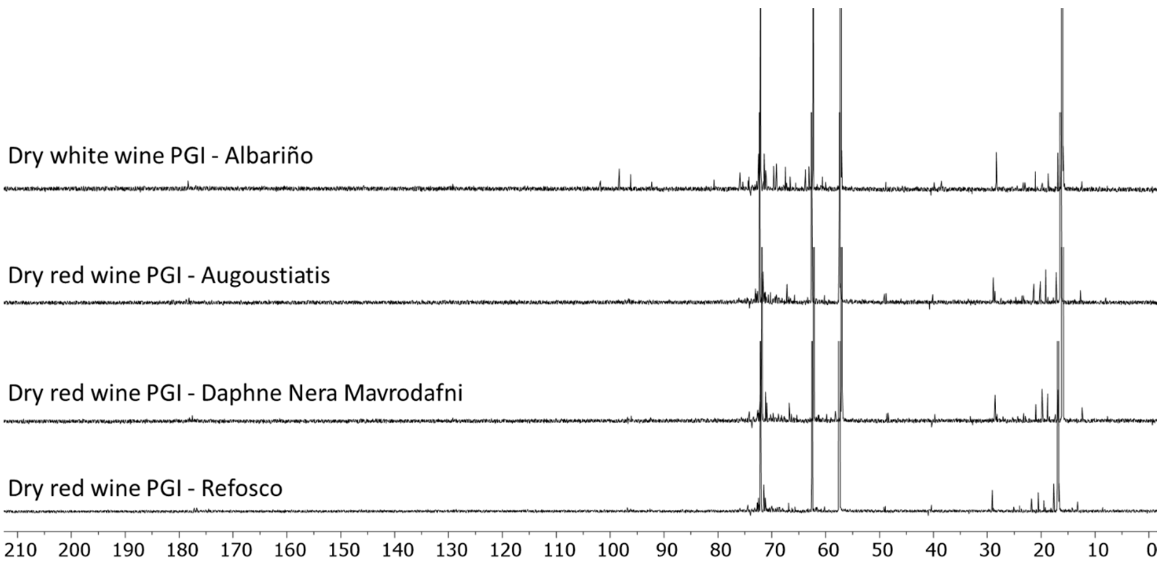

Figure 3. ^{13}C NMR spectra of Ileia wines.

Concerning the wines from Ileia (Figure 3), the three made from red grapes share a very similar ^{13}C spectrum, with no relevant differences. The patterns change for the white Albariño, which has a characteristic group of signals between 90 and 110 ppm.

2.4. Ioannina Samples

Two wines from Ileia were analyzed: one red and one white from, respectively, grapes of the type Vlahiko and Debina (Figure 4).

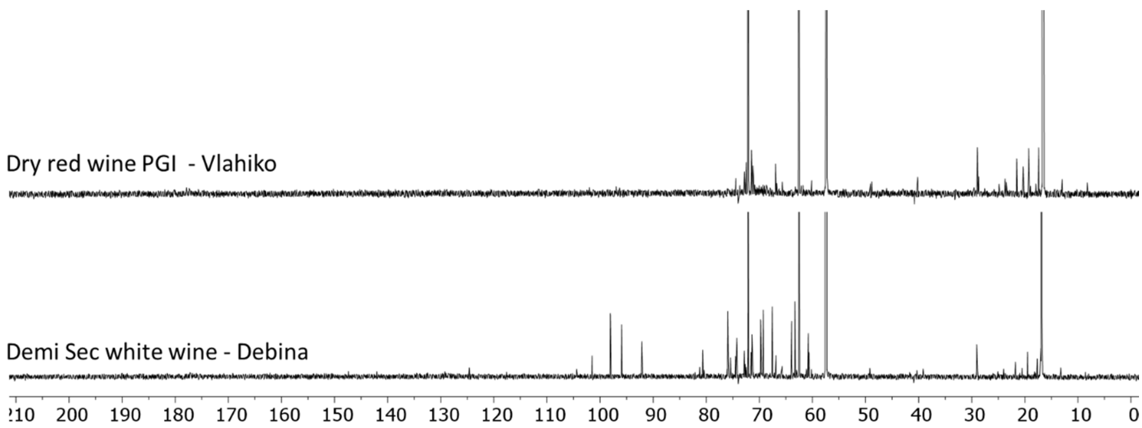

Figure 4. ^{13}C NMR spectra of Zitsa (Ioannina) wines.

Vlahiko and Debina wines from Zitsa (Ioannina) look very different in the ^{13}C NMR spectra. A first important difference is represented by the relative concentration of chemicals; as the samples were analyzed in pure form, the richness of signals and their qualitative intensity are indicative of the relative organic compounds' availability in the wine. In this context, Debina wine is richer in its organic fraction, and important patterns can be observed (Figure 4) especially in the portion ranging from 55 to 82 ppm, and from 90 to 115 ppm.

2.5. Meteora Samples

The three wines considered from Meteora were prepared from grapes Malagouzia and Assyrtiko (white) and Limniona (red). The ^{13}C NMR spectra are reported in Figure 5.

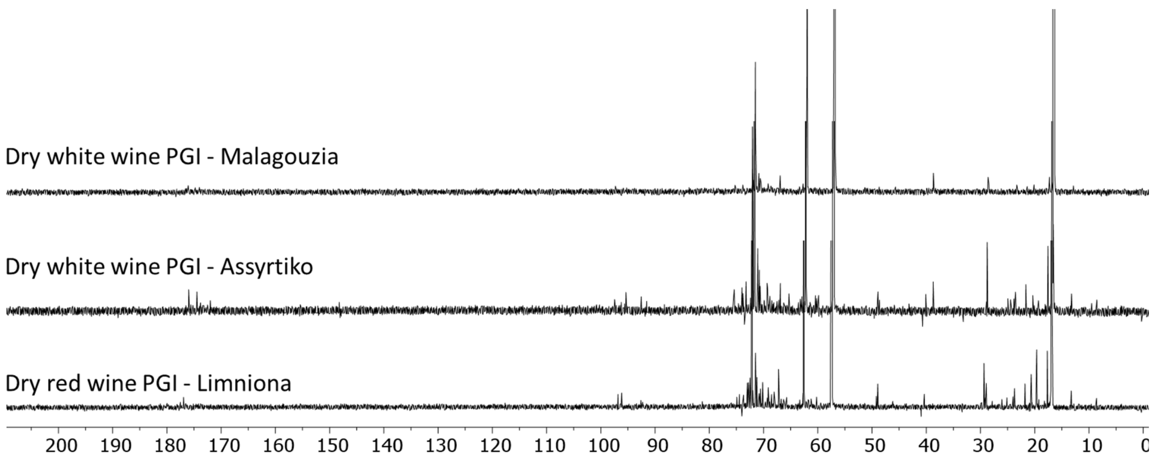

Figure 5. ^{13}C NMR spectra of Meteora wines.

The three analyzed wines from Meteora show different patterns in the ^{13}C NMR spectra. In general, Assyrtiko and Limniona samples seem richer in composition when compared to the Malagouzia wines, suggesting once again that the difference in grapes can be sometimes overwhelmed by the same geographical origin. This qualitative observation sets the basis for a quantitative classification based on geography by means of an appropriate treatment of ^{13}C data with statistics [1].

2.6. Korinthos Samples

Two Agiorgitiko wines (one red and one rosé), and a blended Syrah–Merlot–Cabernet (red) from Korinthos were analyzed (Figure 6).

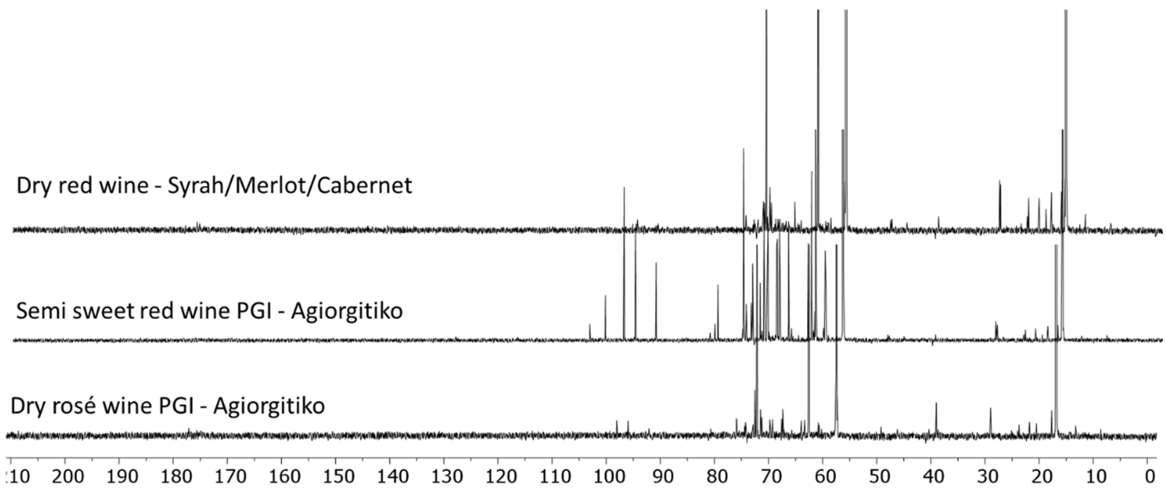

Figure 6. ^{13}C NMR spectra of Korinthos wines.

The ^{13}C NMR spectra of the three samples from Korinthos are different for each sample (Figure 6). Semi-sweet red PGI wine (Agiorgitiko) results are richer in composition, maybe due to the specific preparation process. The ^{13}C pattern registered for the other Agiorgitiko wine (dry rosé PGI) seems a less rich version (in terms of composition) of the sweet red one made from the same grape, as all the relevant signals are common in both samples, with the red sweet wine showing many additional patterns.

2.7. Macedonia Samples

Six samples from Macedonia were considered for analysis: three prepared from mono-varietal grapes (Malagouzia, Syrah, and Xinomavro) and three blended (Syrah–Xinomavro, Xinomavro–Mavroudi–Sefka, Merlot–Xinomavro, Figure 7).

Regarding the Macedonia samples, the monovarietal or the blended nature of the wine does not seem to have been the origin of the differences in their organic composition. Malagouzia, Syrah, Xinomavro, and Merlot–Xinomavro wines show a very similar pattern, which indicates, indeed, a not particularly rich composition. On the contrary, Syrah–Xinomavro and Xinomavro–Mavroudi–Sefka show the presence of several different organic carbons, with comparable patterns.

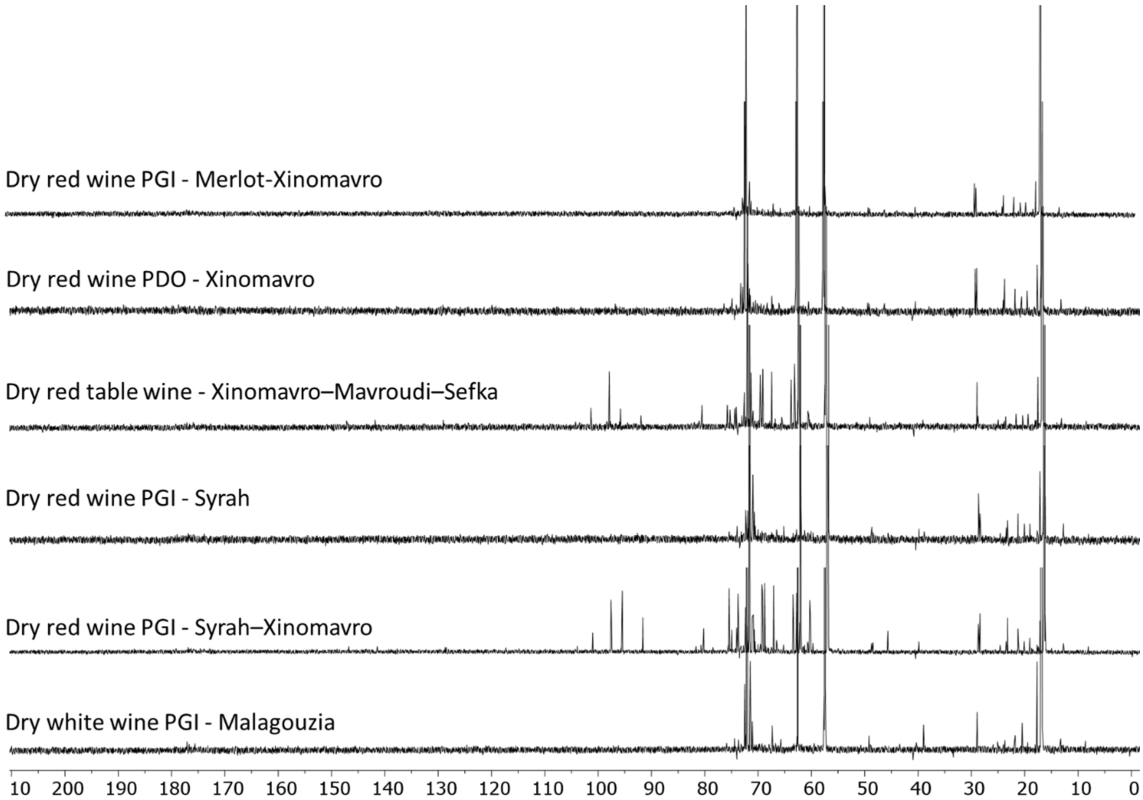

Figure 7. ^{13}C NMR spectra of Macedonia wines.

3. Conclusions

The qualitative analysis of ^{13}C NMR spectra relative to Grecian wines produced from different grapes confirmed the possibility of employing NMR spectroscopy for wine classification. Nevertheless, the different spectral patterns observed can be related to the grape type as well as to the geographical origin. Non-homogeneous trends were observed in samples from the same geographical area. In this context, in order to employ the methodology herein presented to discriminate within different wines, some additional analytical steps need to be performed. More information can be extracted from the ^{13}C NMR spectra by opportune multivariate statistical techniques.

4. Methods

Wine samples were collected from their original bottles and analyzed in pure form (0.4 mL). Proton-decoupled ^{13}C NMR analysis, in the presence of 30 mL of D_2O containing 10% of tetramethylsilane (TMS, internal reference) (Sigma-Aldrich Italy) was then conducted. As TMS is almost insoluble in D_2O, when this reference was not used, the typical signal at 60.1 ppm of glucose, common to all the samples, was taken as an internal reference for scale adjustment [7]. The NMR measurements were taken using a Bruker NEO 500 spectrometer equipped with a 5 mm pulsed-field z-gradient broadband BBFO probe and a variable-temperature unit operating at 125 MHz for the carbon nucleus. The following acquisition parameters were applied for each measurement: time domain 32K, 2500 scans, and a spectral width of 240 ppm. The spectral data from the ^{13}C NMR analysis were processed as follows: Fourier transformation was applied and apodization with an exponent = 0.1 was performed, followed by an automatic baseline and phase corrections. The resulting spectra were studied in the range between 0 and 210 ppm. Spectral manipulation was performed using the Bruker Top Spin software [8].

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Conflicts of Interest: The authors declare no conflict of interest.

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