THE COMPOSITIONAL CHARACTERIZATION OF CADARCĂ WINE BY COMPARISON WITH OTHER ROMANIAN RED WINES USING ^{1}H-NMR SPECTROSCOPY

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În această lucrare este prezentată o modalitate de utilizare a spectroscopiei 1H-RMN pentru determinarea compoziţiei vinului Cadarcă. Cadarcă este un vin tradiţional, fiind produs într-o arie restrânsă din România - Miniş, Crişana şi Recaş. Analiza spectroscopică ^{1}H-RMN cuplată cu procesarea statistică a datelor (Analiza Componenţilor Principali) au fost utilizate pentru caracterizarea vinurilor Cadarcă şi pentru a stabili similitudini sau diferenţe între acest tip de vin şi alte vinuri roşii româneşti de calitate superioara (Fetească Neagră, Cabernet Sauvignon si Merlot).

This paper reports the use of ^{1}H-NMR spectroscopy to determine the composition of Cadarcă wine. Cadarcă is a special wine produced in a limited aria of Romania - Miniş, Crişana and Recaş. ^{1}H-NMR spectroscopic analysis coupled with statistical data processing (Principal Component Analysis) was used to characterize Cadarcă wines and to establish the similarities or differences between this type of wine and other high quality red Romanian wines (Fetească Neagră, Cabernet Sauvignon and Merlot).

Keywords: wine, PCA, ^{1}H-NMR, composition

1. Introduction

Cadarcă wine is a traditional Romanian wine originating from Miniş vineyards and it was produced for the first time in 1744. Cadarcă wine was the preferred red wine in 1750 in the Habsburg court according to the National Inter-professional Organization of Wine-growing from Romania.

Cadarcă wine is produced in the west of Romania, both in Crişana and Recaş vineyards. The wine is produced with addition of raisins and the grape must

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has a sugar content of 150-220 g/L. Cadarcă wine has a color ranging from bright red to dark red, a particular flavor of fresh fruit, full, velvety, sometimes acid and it develops a complex bouquet after 2-3 years. When grapes turn to raisin, the wines obtained are oxidative with cloves flavor and slightly astringent taste [1].

In some earlier studies of Romanian wines, a method used for identification and quantitative measurement of some compounds, usually found in wines, was developed based on ^{1}H-NMR spectroscopy. "Fingerprints" for several Romanian wines have been obtained through identification and quantitative measurement of 14 minor components. These fingerprints were used for establishing wine identity [2-3].

Researchers from all over the world used ^{1}H-NMR spectroscopy coupled with statistical data to characterize and to authenticate their national wines [4-14].

In this study the chemical composition of Cadarcă wines by using ^{1}H-NMR spectroscopy was determined. Based on data provided by the ^{1}H-NMR spectra and using a statistical method (PCA) the similarities and differences between Cadarcă wines and other high quality Romanian red wines were investigated (Fetească Neagră, Cabernet Sauvignon and Merlot).

2. Experimental part

The Cadarcă wine samples subjected to this study were produced in Miniş vineyard in 2003, 2004 and 2006. The high quality Romanian wines examined for comparison with Cadarcă wines were: Fetească Neagră (FN), Cabernet Sauvignon (CS) and Merlot (M) varieties. The originating vineyards and the production years for these red wines are presented in Table 1.

Table 1

Identification data for the red wines used in this study

No.	Type of wine	Symbol	Vineyard	Production year
1.	Fetească Neagră	FN-1	Murfatlar	2007
2.	Fetească Neagră	FN-2	Urlați	2006
3.	Fetească Neagră	FN-3	Odobeşti	2006
4.	Fetească Neagră	FN-4	Valea Călugăreasca	2007
5.	Fetească Neagră	FN-5	Medgidia	2008
6.	Cabernet Sauvignon	CS-1	Urlați	2006
7.	Cabernet Sauvignon	CS-2	Murfatlar	2009
8.	Cabernet Sauvignon	CS-3	Panciu	2009
9.	Cabernet Sauvignon	CS-4	Valea Călugăreasca	2007

10.	Merlot	M-1	Murfatlar	2007
11.	Merlot	M-2	Urlați	2006
12.	Merlot	M-3	Panciu	2009
13.	Merlot	M-4	Valea Călugărească	2007
14.	Merlot	M-5	Medgidia	2007

^{1}H-NMR spectra were recorded on a Varian INOVA 400 spectrometer ("C.D. Nenitescu" Institute of Organic Chemistry, Romanian Academy), operating at 9.4 Tesla, corresponding to the resonance frequency of 399.95 MHz for the ^{1}H nucleus, equipped with a direct detection four nuclei probe head and field gradients on *z* axis. Samples were analyzed in 5 mm NMR tubes (Norell 507). The chemical shifts are reported in ppm, using the TSP as internal standard (10mM). Typical parameters for ^{1}H-NMR spectra were: 45° pulse, 2.05 s acquisition times, 6.4 KHz spectral window, 12 s relaxation delay, 16 scans, 26 K data points. The FID was not processed prior to Fourier transformation. The average acquisition time of the ^{1}H-NMR spectra was approximately 4 minutes. All wines were recorded by using a concentration wine/D_2O = 9/1 (v/v).

The statistic analyses (*Principal Component Analysis*) used to investigate the similarities and differences between Cadarcă wines and the other red wines was carried out using the *XLSTAT* 2010 program.

3. Results and discussions

The method used for marker identification in the ^{1}H-NMR spectrum is similar with the one described in earlier studies.[2,15,16] Some of the markers identified for Cadarcă wine produced in Miniş vineyard in 2003, which have been used for quantitative measurement of different compounds in ^{1}H-NMR spectra are exemplified in Fig. 1.

Although the NMR method is commonly used for qualitative determinations, it can be used as well for quantitative measurements. Following that idea we applied NMR method for quantitative measurements using TSP added in the deuterated solvent (D_2O) in a known amount (10mM/L). In this way the concentration of various compounds in Cadarcă wines and in other red wines such as Fetească Neagră (FN), Cabernet Sauvignon (CS) and Merlot (M) were measured.

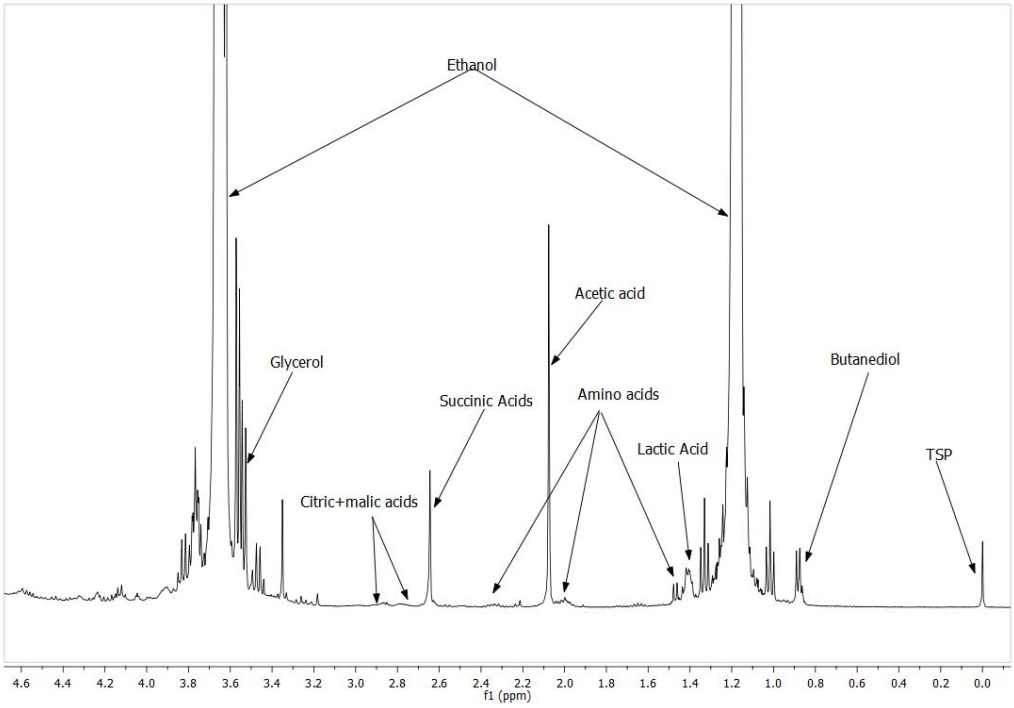

Fig. 1 ^{1}H-NMR spectrum of Cadarcă wine produced in 2003

Table 2 displays the chemical composition of several compounds thus determined in the Cadarcă wine.

Table 2

Major components (mM/L) in Cadarcă wines

No.	Compounds (mM/L)	Cadarcă wine 2003 (CA-1)	Cadarcă wine 2004 (CA-2)	Cadarcă wine 2006 (CA-3)
1.	Lactic Acid	5,38	5,14	5,35
2.	Acetic acid	17,45	20,30	19,91
3.	Succinic acid	7,68	10,05	8,38
4.	Malic acid	8,65	9,01	7,66
5.	Citric acid	0,01	0,01	0,02
6.	Tartric acid	5,15	6,91	4,86
7.	Glycerol	125,05	134,14	112,16
8.	Amino acid 1	5,95	5,74	5,92

9.	Amino acid 2	1,47	2,27	2,25
10.	Amino acid 3	4,98	4,44	5,56
11.	Poliphenols	35,95	40,90	43,42

The amount of various compounds quantitatively measured using ^{1}H-NMR method represents the raw data in the statistical study. *Principal Component Analysis* method (PCA) was used as the classification technique. Table 3 contains the chemical composition of the Fetească Neagră, Cabernet Sauvignon and Merlot wines used for the comparison with Cadarcă wines.

Table 1

Major components (mM/L) in Fetească Neagră (FN), Cabernet Sauvignon (CS) and Merlot (M) wines

No.	Compounds (mM/L)	FN-1	FN-2	FN-3	FN-4	FN-5	CS-1	CS-2
1.	Lactic Acid	14,44	20,21	17,81	13,75	14,20	16,37	17,93
2.	Acetic acid	12,85	12,25	13,60	13,21	12,31	11,65	10,86
3.	Succinic acid	9,03	8,99	9,28	8,69	6,89	8,09	8,63
4.	Malic acid	6,85	7,30	2,25	6,88	7,26	3,54	3,06
5.	Citric acid	0,01	0,01	0,00	0,00	0,00	0,02	0,00
6.	Tartric acid	11,94	12,57	11,35	11,42	11,77	8,72	8,71
7.	Glycerol	156,76	156,49	172,70	157,21	159,37	118,74	185,86
8.	Amino acid 1	1,02	2,43	3,09	1,98	1,90	2,16	2,57
9.	Amino acid 2	1,93	2,07	1,92	2,37	1,95	1,95	1,08
10.	Amino acid 3	11,83	11,56	12,22	11,09	11,76	13,21	13,30
11.	Polyphenols	58,29	59,91	71,98	58,20	54,39	35,39	35,23

Major components (mM/L) in Fetească Neagră (FN), Cabernet Sauvignon (CS) and Merlot (M) wines (continued)

No.	Compounds (mM/L)	CS-3	CS-4	M-1	M-2	M-3	M-4	M-5
1.	Lactic Acid	15,86	18,47	17,35	20,54	27,75	17,39	23,89
2.	Acetic acid	10,73	12,10	11,56	12,86	12,46	11,56	13,21
3.	Succinic acid	8,00	7,84	10,75	10,95	12,03	8,75	8,02
4.	Malic acid	5,68	2,25	3,05	2,44	3,60	5,05	2,00
5.	Citric acid	0,00	0,00	0,00	0,00	0,00	0,00	0,00

6.	Tartric acid	7,70	7,84	9,43	8,10	7,29	12,43	9,23
7.	Glycerol	189,64	118,65	165,77	168,47	168,65	167,20	174,95
8.	Amino acid 1	2,80	1,92	2,61	2,79	2,55	2,43	2,53
9.	Amino acid 2	1,00	1,92	2,29	2,03	2,21	2,39	1,71
10.	Amino acid 3	12,32	11,41	12,17	14,35	16,40	11,17	13,77
11.	Polyphenols	31,17	34,45	36,60	32,34	36,13	38,66	35,23

Fig. 2 exhibit the average composition of organic acids in Cadarcă wine by comparison with the other high quality red wines studied. It can be observed that Cadarcă wine has the smallest quantity of lactic and tartric acids compared to the other red wines and the largest amount of acetic and malic acids. All wines have approximately the same amount of succinic acid.

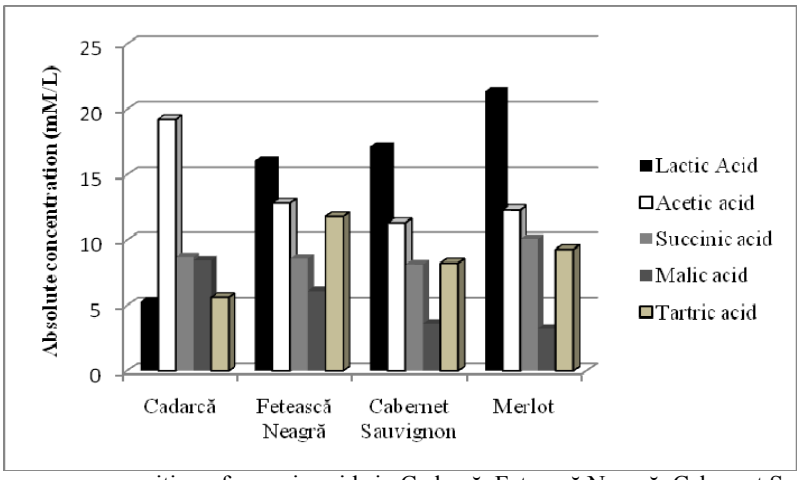

Fig. 2 Average composition of organic acids in Cadarcă, Fetească Neagră, Cabernet Sauvignon and Merlot wines

Fig. 3 shows the average composition of polyphenols and glycerol in Cadarcă wine and in the other red wines examined. All red wines have similar average amounts of polyphenols. A slightly larger amount of polyphenols was measured in Fetească Neagră wines. Regarding the quantity of glycerol obtained for the studied wines, it can be concluded that the concentration of glycerol is lower in the Cadarcă wine compared to the other red wines, but it is situated in the range described in literature (50-220 mM/L).

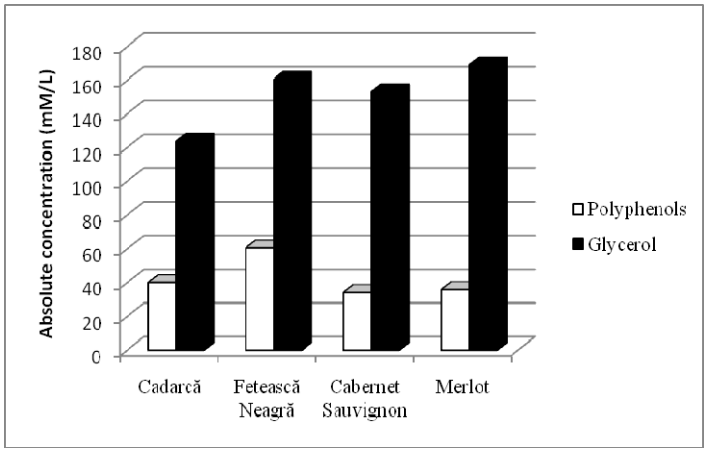

Fig. 3 Average composition of polyphenols and glycerol in Cadarcă, Fetească Neagră, Cabernet Sauvignon and Merlot wines

Fig. 4 illustrates the representation of principal component scores F1/F2 for Cadarcă wines and the red wines examined. It can be observed that Cadarcă wines group is distinctive, being obviously separated from the other red wines Fetească Neagră, Cabernet Sauvignon and Merlot.

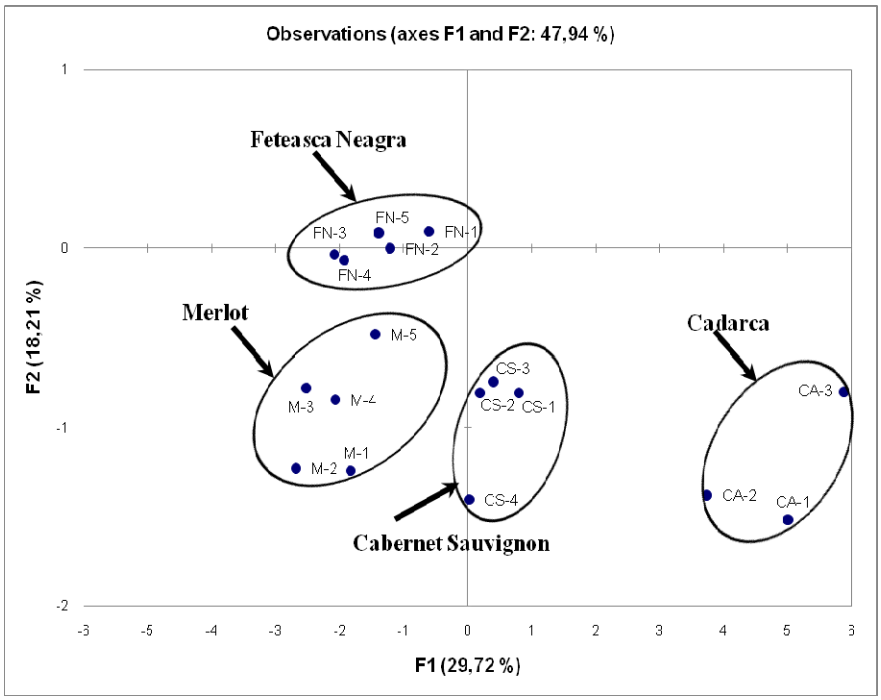

Fig. 4. Principal component (factor) scores F1/F2 plot for Cadarcă (CA) wines and other red wines (Fetească Neagră – FN, Cabernet Sauvignon – CS and Merlot – M)

Therefore, the ratio between various compounds in Cadarcă wines results in a unique "fingerprint" for this wine which allows a good separation of this wine variety from the others red wined analyzed in the present study.

6. Conclusion

The chemical composition of Cadarcă wines and other Romanian high quality red wines was established by means of ^{1}H-NMR spectroscopy. Statistical analysis of the data allowed a good differentiation of Cadarcă wines from the other wines.

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