Determination of Wine Aroma Compounds by Head Space "In tube extraction" Technique and Gas Chromatography (HS-ITEX-GC/MS)

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ABSTRACT

This study investigates the influence of vintage on the aroma compounds of white wine Episcopal from vineyard Ciumbrud, located in central Transylvania, by a non-destructive head space in tube extraction technique in tandem with GC-MS. The samples selected for analysis come from three consecutive years (2009, 2010 and 2011) from Episcopal assortment, a high quality wine obtained by blending three types of wine varieties: Sauvignon Blanc, Traminer and Pinot Gris. The results reflect the compositional similarities but also the influence of vintage on the composition of wine aroma compounds. Results showed significant similarities between the composition of major compounds, 2-methyl-1-butanol, butanoic acid ethyl ester, hexanoic acid ethyl ester, octanoic acid ethyl ester, which together account for over 50% of the compounds identified. Significant differences appear both on the number of identified compounds in wine harvest 2010 compared to the other two years as well as through differences in concentration of two compounds: 3-methyl-butanol and 2,4-hexadienoic acid ethyl ester.

Keywords: *white wine, aroma compounds, vintage influence, HS-ITEX-GC/MS.*

INTRODUCTION

The composition of volatile compounds from wine is one of the most complexes from many others food products and is dependent on the type of wine, grapes, fermentation and ageing processes. Several hundred volatiles compounds have been identified in wine, belonging to different chemical classes. The most important classes of volatile compounds in wines are higher alcohols and esters, also carbonyls are present, acids, terpenes, norisoprenoids, sulphur compounds and pyrazines (Henryk and Szczurek, 2010).

The concentration of volatile compounds usually present in wine are ranging from mg/L down to a few ng/L. In the analysis of key odorants from wine and from many food matrices by GC-MS and gas chromatography – olfactometry, the steps of extraction, pre-concentration, detection and quantification process, especially of the compounds present in trace concentrations pose a serious analytical challenge (Guth 1997; Siebert et al. 2005; Socaci et al. 2012; Salanţă et al. 2012). Different sampling techniques are used for the isolation of wine and grapes volatile compounds, usually liquid/liquid extraction, static headspace, dynamic headspace, solid phase extraction (SPE), in tube extraction (ITEX), stir bar sorptive extraction (SBSE) and solid phase microextraction (SPME) (Ortega-Heras et al. 2002; Piñeiro et al. 2004; Peña

et al. 2005; Henryk and Szczurek, 2010; Socaci et al., 2012). In this respect, In-tube extraction (ITEX) is a novel technique that can be coupled with gas chromatography mass-spectrometry (GC-MS) and used for the extraction and separation of volatile compounds from wine in order to determinate the compositional differences between different wine sorts.

The chemical components of wine are derived from multiple sources; during fermentation grape flavour components are extracted into the wine and new compounds are formed by numerous chemical and biochemical processes (Robinson et al., 2014). The conditions of climate vary from year to year and it is commonly accepted worldwide that vintage has a major influence on fruit composition. Studies of aroma composition of Sauvignon Blanc (Sefton et al. 1994) and Merlot Noir (Kotseridis et al. 1998) have confirmed this observation on an analytical level.

MATERIALS AND METHODS

The aim of the present study was the identification of aroma compounds for a variety of white wine, Episcopal, obtained by blending varieties Pinot Gris, Traminer and Sauvignon Blanc, obtained from Ciumbrud vineyards area (central Transylvania) harvest in three years (2009, 2010 and 2011). The analyses followed the separation and identification of wine aroma compounds by HS-GC-MS-ITEX technique.

ITEX analysis

The extraction of volatile compounds from white wine samples was performed using the ITEX technique in accordance with method developed in the Laboratory of Food Quality and Safety from Food Science and Technology Faculty UASVM Cluj-Napoca (Socaci et al., 2012 and Salanta et al., 2012). The main method parameters are: incubation temperature (60°C), incubation time (20 minutes), number of strokes (30), syringe temperature (60ºC), agitation speed (500 rpm), extraction volume (1000 µL), extraction speed (100 µL/s), desorption temperature (200ºC), trap cleaning temperature (250ºC), trap cleaning time 2 min with N_2. The used ITEX fibre was an ITEX-II Trap (G23)-SilicoNert 2000, Tenax TA 80/100 mesh, ea, fibre. After incubation a 250 µL headspace sample was injected in the GC-MS injector. All samples were analyzed in duplicate.

GC-MS analysis

The analyses were carried out on a Shimadzu GC-MS QP-2010 (Shimadzu Scientific Instruments, Kyoto, Japan) model gas chromatograph-mass spectrometer equipped with a CombiPAL AOC-5000 autosampler (CTC Analytics, Zwingen, Switzerland). A Zebrone ZB - 5ms column of 50m x

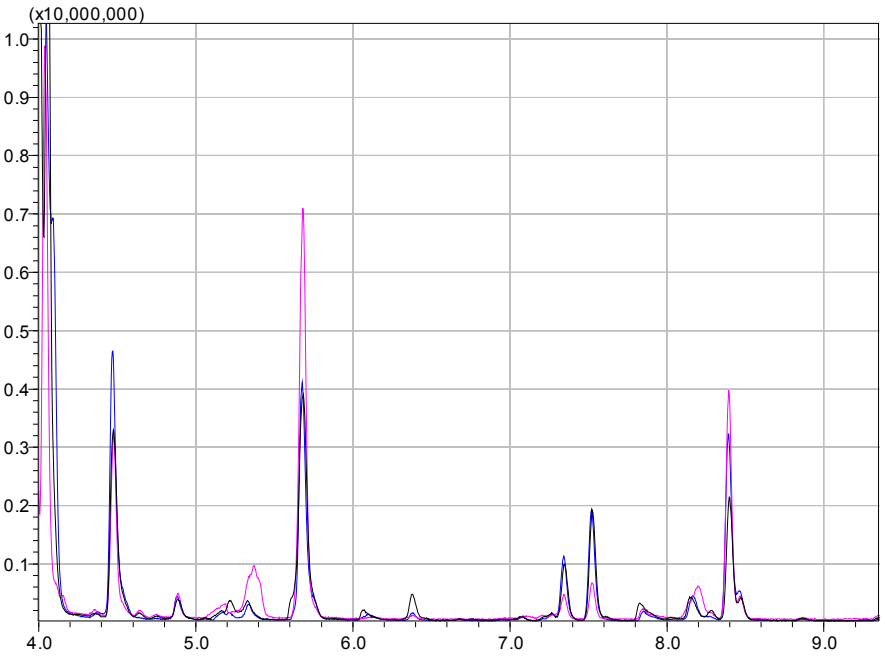

Fig. 1. The chromatogram for white wine Episcopal 2009, 2010 and 2011

0.32 mm i.d. and 0.25 µm film thickness was used for the analyses. The parameters for the method were: injector temperature 250.0ºC; split ratio 1:200, carrier gas-helium 1.39mL/min, detector MS, ion source temperature 250.0ºC, interface temperature 250.0ºC, MS mode EI, scan range 50-400u, scan rate 2000u/s. The program for column oven temperature was: 60ºC (3 min) to 160ºC at 3ºC/min to 250ºC (10 min). Approximately 1 ml of wine was used for the analysis, which economizes storage space and reduces the time needed for sample preparation.

The identification of volatile compounds was carried out by comparing the mass spectra obtained with NIST27 and NIST147 library information and verified by comparison with retention indices drawn from www.pherobase.com or www.flavornet.org (for columns with a similar stationary phase to the ZB-5ms column).

RESULTS AND DISCUSSION

Figure 1 and Table 1 presents the results obtained after the separation by ITEX-GC/MS technique of aroma compounds in Episcopal (Ep)

Tab. 1. Aroma compounds determined by HS-ITEX-GC/MS in the white wine Episcopal in the three years vintage

No. pic	Compounds	R.T. (min)	% Area / Vintage		
			Ep-2009	Ep-2010	Ep-2011
1	3-Methyl-1-butanol	4.03	-	-	12.75
2	2-Methyl-1-butanol	4.10	11.84	15.57	3.475
3	2-Methyl propanoic acid ethyl ester	4.47	7.73	7.32	10.055
4	Acetic acid,2-metilpropilester	4.92	0.63	0.8	
5	Butanoic acid ethyl ester	5.71	10.655	18.61	9.455
6	Lactic acid ethyl ester	6.06	0.725	-	-
7	2-Metil butanoic acid ethyl ester	7.34	1.745	0.84	2.28
8	3-Metil butanoic acid ethyl ester	7.55	3.67	1.42	4.0
9	1-Hexanol	7.83	0.45		1.015
10	3-Methyl-1-butanol acetat	8.39	4.265	2.035	6.71
11	2-Methyl-1-butanol acetat	8.47	0.655	0.74	1.01
12	2-Eteniltetrahidro-2,6,6-trimethyl-2H-Pyran	12.14	1.15	-	0.73
13	3-Decyne	12.99	1.04	-	-
14	Hexanoic acid ethyl ester	13.41	17.22	28.89	21.105
15	3-Undecyne	13.63	0.655	-	0.77
16	o-Cymene	14.41	0.255		
17	Limonene	14.60			0.24
18	2,4-Hexadienoic acid ethyl ester	17.51	19.93	-	3.255
19	Butandioic acid di-ethyl ester	20.75	0.55	-	0.22
20	Octanoic acid ethyl ester	21.45	12.205	20.825	18.645
21	1.2-Dihidro-1.1.6-trimetilnaftalen	27.25	0.6		
22	Decanoic acid ethyl ester	28.67	1.155	1.44	1.87
	Total % aria		97.125	98.49	97.585
	Total No. compounds		20	11	17

wine assortment, obtained in 3 years of production. As shown in Table 1, were identified a total of 22 aroma compounds, respectively 20 in Ep-2009, 11 in Ep-2010 and 17 in Ep-2011.

From the total compounds identified, a number of 4 compounds are in majority, each with more than 10% and holding together over 50% of the total percentages of area. The major compounds which are found in all three investigated years are: 2-methyl-1-butanol, butanoic acid ethyl ester, hexanoic acid ethyl ester, octanoic acid ethyl ester, which, although they are present in each of the samples shows the variations rather important, especially in the case of 2-methyl-butanol. The compositional differences occur mainly for wine obtained in 2010 which showed the lowest number of compounds, about half of those identified in 2009. A particular case is represented by the wine produced from 2011 harvest where compound 3-methyl-butanol was identified in a significant percentage of area (12.75%), compound which is not present in other samples from previous years.

A special case is also 2,4-hexadienoic acid ethyl ester, compound that occurs in very high concentrations in the harvest of 2009 (19.93% percent of area), in a low concentration (3.25% percent of area) in 2011, but has not been identified for 2010 harvest. These differences show that although Episcopal assortment of wine is produced through a process similar in all the three years, compositional differences that occur are due to the different accumulation of aroma compounds, which is influenced by fluctuations in annual climate. Results are in agreement with the literature data regarding the influence of climate on aroma compounds of grape and wine composition.

CONCLUSION

The identification of aroma compounds for a variety of white wine, Episcopal, obtained by blending varieties Pinot Gris, Traminer and Sauvignon Blanc, obtained from Ciumbrud vineyards area (central Transylvania,) harvest in three years (2009, 2010 and 2011) was achieved through a modern and non-destructive technique namely ITEX-HS-GC/MS. The obtained results showed significant similarities between the composition of major compounds, 2-methyl-1-butanol, butanoic acid ethyl ester, hexanoic acid ethyl ester, octanoic acid ethyl ester, which together account for over 50% of the total compounds identified. Significant differences arising on the number of identified compounds in wine from 2010 harvest compared to the other two years, in which the number of identified aroma compounds was half of those occurring in the last two years. Two particularly interesting cases were observed for 3-methyl-butanol and 2,4-hexadienoic acid ethyl ester compounds. Thus, 3-methylbutanal in 2011 reaches 12.75% (percent of area) while in the other two years was not identified, and the 2,4-hexadienoic acid ethyl ester appears in high concentration (19.93%) in 2009, for 2011 appears in a much lower percentage (3.25% of the area) and in 2010 was not identified.

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