### Journal of Applied Botany and Food Quality 86, 104 - 112 (2013), DOI:10.5073/JABFQ.2013.086.015

<sup>1</sup>Department of Food Chemistry and Nutrition, Faculty of Food Science, Corvinus University of Budapest, Budapest, Hungary <sup>2</sup>Department of Enology, Faculty of Food Science, Corvinus University of Budapest, Budapest, Hungary

# GC-MS Description of the primary aroma structure of two Kadarka wines considered indigenous in Hungary

Mariann Csóka<sup>1</sup>, Mária Amtmann<sup>1</sup>, Diána Ny. Sárdy<sup>2</sup>, Miklós Kállay<sup>2</sup>, Kornél Korány<sup>1\*</sup>

(Received May 17, 2013)

# **Summary**

Two high quality Kadarka wines of the Great Plains of Hungary and Szekszárd terroirs were thoroughly analysed by GC-MS measurements subsequent to a two step sample preparation method elaborated at our Department. The goal of the work was to describe the varietal relative aroma-picture of the Kadaraka species considered indigenous in Hungary. The relative aromagram construction method creates the possibility of studying the scent features by chemical classes separately. The data prove that the primary aromaspectra beside certain smaller similarity differ to a reasonable extent due to the habitats of origin. The Kadarka of the poorer sand soil of the Great Plains is more fragrant than that of the loess of Szekszárd. The analytical results are supported by the organoleptic experience as well.

### Introduction

The Kadarka variety of *Vitis vinifera* L. is considered indigenous in Hungary. In the centuries XVII-XIX<sup>th</sup> it was the most widely spread blue grape species in the country. At the beginning of the 1800's years more than two third of the red vine plantations consisted of it. The most characteristic attribute of Kadarka wine is its piquancy. It is a highly fragrant, fruity and slim wine. Unfortunately, in the middle of the last century the intensive mechanization of vine growing made its production dramatically decrease due to this cultivated variety's capability of being merely hand-cultivated. Modish "worldwide" spreading species made the case worse, thus nowadays this traditional Hungarian variety almost has to be discerned again.

Recently Kadarka as one of the *Hungarics* (*i.e.* gastronomic uniquenesses) starts to live its new *renaissance*. The provenance of this grapevine is not known exactly. Some experts originate the name from Skutari what is the Asia Minor part of Istanbul called Üsküdar in Turkish and Skaderi in the Serbian and Croatian languages (ÚJVÁRI, 2007). Certain conceptions think it derives from the environs of Skhodari-lake (Albania), others consider Kadarka to come from Asia Minor (TAKLER, 2004). It is more than likely that in the XVI. century the Serbs escaping from the Turks brought it into Hungary through the Balkan. Later, having retaken the fortress of Buda from the Turks and Serbian refugees been settled down on the depopulated lands, the Serbs were the ethnic who started spreading this cultivated variety (cv.) in large scale on the emptied parts of the country. The synonyms of Kadarka are "Negru" in Romania and "Gamza" in Bulgaria (JANYIK, 2010).

After the phylloxera vine-pest in 1875 Kadarka was planted in sandy soil only, thus by 2002 its ratio decreased to 1.1 % compared to the former 67 % at the beginning of the 19<sup>th</sup> century. In 2007 European Danube-Maros-Tisza-Körös Region elected this wine as an Euro-Region wine thus Hungary, Romania and Serbia, the three countries involved in the production agreed upon the details (registration of the producers, cultivation mode, character formation and legislation) of trade (JANYIK, 2010).

In the last 3-5 years valuable and interesting articles of importance were published on the fragrance features of red wines considered rather "scentless" by the literature, previously. Most of them is connected to the modern and fashionable SPE (GÓMEZ et al., 2011 and 2012) and head-space SPME sample preparation methods (VEVERKA et al., 2012) that are rarely sensitive and selective to the varietal constituents enough, therefore are hardly sufficient for grabbing the cultivated variety's character. The latter paper reports good results on the terpenoid distribution and volatile phenolics of the distillates of 16 red wines but spirits are not the wines themselves, brandy-distillation may seriously distort the ratios of the volatiles making them unfit for cv. description. Traditional liquid-liquid extraction methods (PERESTRELO et al., 2006) catch all kinds of substances not only the volatile, gas chromatographically measurable ones, thus the main compounds of the wines depress those bouquet components that are important in describing the varietal scent features (IVANOVA, et al., 2012).

Our present work intends to give an overall picture of the bouquet structure of the barely known Kadarka wine through the GC-MS investigation of two high quality Kadarka representatives deriving from the Great Plains and the famous red wine producing Szekszárd region of Hungary.

### Materials and methods

### Samples

Two high quality (appellation d'origine vin délimité de qualité supérieure, AOVDQS) Kadarka wines of the 2011<sup>th</sup> year vintage have been analysed by courtesy of the excellent wineries Koch in the Great Plains (Kiskörösi Kadarka) and Vida (Szekszárdi Kadarka) in the red wine producing Szekszárd region of Hungary.

The terroir of Great Plains is the largest one of Hungary. Its size is 27 900 hectares. At least one fourth of the Hungarian wines are produced here. Its climate is extreme, hard winter frosts are common and the summers are hot and dry. The soil is dominantly immune sand. Among the wines deriving from here white, rosé and red ones can equally be found. They are light and mild and of table quality generally. The most well-known representative of them is the Kadarka of Kiskörös (EPERJESI et al., 2003).

The Szekszárd terroir extends in the county of Tolna with a size of 6000 hectares of loess soil and temperate climate. This land became famous for its Kadarka wines. Kadarka *cv*. grapevine brings outstanding quality grapes under the warm weather and brilliant aeolian soil conditions of this region. The wines of this area are flavoured and tasty and have bright colour. They are mild, piquant and pleasantly acidic. The white wines of the region are aromatic and full-bodied, but due to the warmth of the climate may suffer from the lack of acids frequently (EPERJESI et al., 2003).

### Sample preparation

In the present work a two step sample preparation procedure has been elaborated at our Department of Food Chemistry and Nutrition.

### 1. Liquid-liquid extraction (LLE) subsequent to distillation (called ,,classic" further)

Prior to distillation 150 ml undecanol-1 internal standard (ISTD) of 0.8 mg/ml concentration in ethanol has been added to 500 ml wine sample (containing 100 g of analytical grade NaCl to obtain ,,salt-out" effect) then poured into a 1000 ml round bottom flask and distilled till 100 ml condensate gathered. The operation has been repeated three times, the fractions ( $3 \times 100$  ml) were collected and fused. The unified condensates were filled into a separation funnel, 15 g of NaCl were added to them and they were extracted three times with 80 ml n-pentane of special purity. Then the extracts were fused and dried on anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated to 1 ml end-volume by evaporation. Into the GC-MS instrument 1 ml of the concentrate has been injected.

# 2. Likens-Nickerson simultaneous distillation-extraction (LN-SDE)

The  $3 \times 400$  ml distillation rest of the previous step was collected, fused and completed with 300 ml distilled water that contained 60 g of analytical grade NaCl. This time 450 ml undecanol-1 internal standard of the above concentration has been added to the mixture. Then the sample was poured into a round bottom flask of 2000 ml, connected to an LN-SDE equipment and distilled against 150 ml of n-pentane of special purity for 1.5 hours after boiling up. Then the pentane extract was put into a refrigerator to freeze out the water content and the dry extract was evaporated to 1 ml end-volume. One microliter of this sample has been introduced into the GC-MS instrument.

### **GC-MS** analysis

Abundance

0

5.00

10.00

15.00

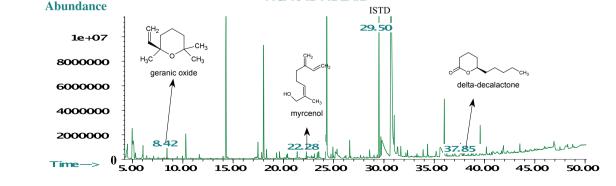
An HP 5890/II gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) equipped with a 60 m  $\times$  0,25 mm  $\times$  0,25  $\mu$ m AT-WAX

fused silica capillary column and a 5971/A mass selective detector (MSD) was used to analyse the volatile compounds of wine extracts. The initial oven temperature was 60 °C and immediately increased to 280 °C at a rate of 4 °C/min. The injector was operated in splitless mode at 270 °C, with a 100:1 split ratio at 0.1 min. delay time. The MSD was run in electron impact mode (70 eV) at 280 °C. Helium (4.6) was used as a carrier gas with the flow rate of 30 cm/s. The detection was performed in the 35-350 mass range at 390 mass/s scan speed. The identification of the fragrance constituents were accomplished using the NBS49k.L, Wiley138.L, Wiley275.L and NIST05.L spectrum libraries. The identification was based on the match quality, programmed temperature retention index measurement (KORÁNY et al., 2006), and retention-time/ reference spectral data of standards if they were available.

#### Results

In our former works (KOVÁCS et al., 1999; KORÁNY et al., 2000) only one step sample preparation was applied as described the above chapter *"1. liquid-liquid extraction subsequent to distillation*". Later the fine, balmy scent of the discarded distillation rest was discerned and decided to be subjected further investigation by LN-SDE. The result is shown in Fig. 1 that depicts two total ion chromatograms (TICs) of the Kadarka wine of Szekszárd.

The chromatograms clearly prove that the distillation remainder after expelling the ethanol constituent of the wine and collecting water condensate of approximately equal volume to the alcohol content, still holds *cv*. characterising primary compounds of importance (*e.g.* geranic oxide or myrcenol among many others) and substances of high scent activity, that is of low odour threshold (delta-decalactone for instance). In addition many of them (including the precedents too) can be measured only in the LN-SDE fraction that we call *alcohol free water-phase*.



25.00

TIC: KADVIDLN.D

TIC: KADVIDCL.D

ISTD

30.00

35.00

40.00

45 00

50.00

Fig. 1: The TICs of the Szekszárdi Kadarka wine samples, simple distillation followed by LLE extraction (upper), LN-SDE extract (lower)

20.00

The gas chromatographic separation was followed by a thorough, manual mode, compound by compound identification of the detected constituents. The number of the identified odorants were 122 in Kiskörösi Kadarka (Great Plains) and 143 in Szekszárdi Kadarka. The tabular statement from the amount of compounds is reported in Tab. 1. The recognised components sorted into chemical classes of decreasing odour activity and species characterising significance are introduced in Tab. 2 in the order of elution. Instead of retention times the **p**rogrammed **t**emperature **r**etention **in**dices (linear retention indices in older term, LRIs) are used to describe the elution sequence. They were measured as discussed in one of our previous articles (KORÁNY et al., 2005).

The mode of typing carries information as follows: The chemicals in **boldface** are present in both Kadarka samples in both fractions (classic and LN-SDE). Compounds in "\*typeface" occure only in the extracts of the *classic* preparation method in one wine. Components of "\*typing" occur in both wine samples but only in the *classic* phase. Substances of "^letters" can be found only in the *LN-SDE* extracts of one sample. Constituents of "^typeface" appear in both wines, but only in the *LN-SDE* phase. Names of "normal" typing are present in both *classic* and *LN-SDE* extracts but only in one of the wines. In the cases of "(name !)"-s the match quality is high enough (roughly 90 %) but the retention data (PTRI) contradicts the chemical structure reported. In these instances of misidentification the names were kept as working designations.

Studying the results in the form of a table that is so complex than Tab. 2 is really exhausting. Therefore relative aromagrams called aroma-spectra have been constructed by measuring the PTRIs and calculating the relative intensities related to the undecanol-1 ISTD. The classification of the identified components into chemical classes creates the chance of the fast comparison of the scent constituents of different origin *i.e.* primary, secondary, tertiary (and/or quaternery). Thus any of the important bouquet sources for example the cv. characterising, the fermentation induced, the maturation or bottle-ageing ones can equally be examined with ease by picking out the group in question. For setting an example Fig. 2 depicts the

total and the primary aroma-spectra of the investigated wines. While Fig. 1 and 2 make the enologists capable of investigating the aroma features of any origin (i.e. *primary, secondary, ... etc.*) with compound by compound details it is almost impossible to form an overall picture of the similarity or the measure of the dissimilarity of the examined wine samples. The block diagram-like processing of the data in Tab. 2 according to the chemical classes gives the chance of the direct comparison as shown in Fig. 3.

## Discussion

The detailed GC-MS analysis subsequent to the two step sample preparation suggested the fairly similar character of the Kiskörösi Kadarka (Great Plains) and the Szekszárdi Kadarka (red vine growing region of Szekszárd) wines. Inspite of the cultivated varieties' identity significantly smaller discrepancies of the total aroma pictures were observed than presumed considering the enormous quality difference between the immune sand soil of the Great Plains and the mild aeolian loess of the Szekszárd region.

The Kiskörösi and Szekszárdi wines scored 7926 and 9325 points of relative intensity expressed in the undecanol-1 ISTD, respectively. This difference of approximately 15 % is not much if the higher fatty acid and benzene and ~relatives content of the Szekszárdi Kadarka is considered. The greater fatty acid level (by nearly 50 %) has relatively little effect on organoleptic features because it recruits mainly from caproic (C<sub>6</sub>), caprylic (C<sub>8</sub>) and capric (C<sub>10</sub>) acids of moderate sensory activity (BURDOCK, 2010).

In the chemical division of "Benzene and ~derivative compounds" not only the b-phenylethyl alcohol content (a fermentation product) is more abundant in the Szekszárdi Kadarka than in the Kiskörösi wine, but nine constituents of importance appear only in the latter. They are as follows: 1317, ^1,2,3-trimethylbenzene, 0.02 %; 1620, \*(R\*,R\*)-(.+-.)-1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-benzene, 0.08 %; 2046, \*p-ethylguaiacol, 0.01 %; 2127, ^1-[6-Hydroxy-2-methyl-3-(1-methylethyl)phenyl]-ethanone, 0.06 %; 2127, ^1-

Compound group	Great Plain			Szekszárd		
	classic	LN-SDE	in both extracts	classic	LN-SDE	in both extracts
Terpenes, sesquiterpenes and relatives	13	32	8	20	25	13
Compounds of benzene ring	5	16	4	9	17	3
S-containing compounds	2	2	2	3	3	2
Acetals	5	2	2	5	3	2
Alcohols, aldehydes, ketons	10	4	2	21	4	3
Furans, O-heterocycles	2	3	-	4	3	1
N-containing constituents	-	1	-	-	1	-
Lactones	5	3	3	2	1	1
Indenes	-	2	-	1	2	1
Constituens of naphthalene skeleton	1	3	1	1	7	1
Esters of fatty acids	23	9	8	27	8	6
Fatty acids	4	4	3	7	5	3
Hydrocarbons	4	1	1	2	2	2
Total	74	82	34	102	81	38

**Tab. 1:** The number of the identified compounds in Kadarka wines

# Tab. 2: The identified components of the Kadarka wines

		G. Plains	Szekszárd
PTRI	Compounds	Area %*	Area %*
	Terpenes, sesquiterpenes and relatives		
1079	^1-acetyl-4-methylbicyclo[3,1,0]hexan-3-one	0.01	
1090	^(+-)-2,6,6-trimethyl-2-vinyl-tetrahydropyran (geranic oxide)	0.1	0.06
1112	^1,5,5,6-tetramethyl-1,3-cyclohexadiene (alpha-pyronene)	0.26	
1128	^p-mentha-2,4(8)-diene(isoterpinolene)	0.03	0.01
1129	*3-methylene-1,5,5-trimethylcyclohexene		0.01
1175	l-limonene	0.03	0.02
1179	^herboxide I	0.01	0.01
1200	^cis-ocimene	0.01	
1211	^2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofuran(ocimene quintoxide)	0.02	0.03
1257	^terpinolene (d-terpinene)	0.01	0.01
1433	cis-linalool oxide	0.25	0.16
1446	^1,2,3,4-tetrahydro-1,1,6-trimethyl-naphthalene (alpha-ionene)	0.03	
1465	trans-linalool oxide	0.1	0.08
1466	*neroloxide		0.01
1541	vitispirane I	0.22	0.15
1544	vitispirane II	0.34	0.38
1544	<u>^linalool</u>	0.01	0.11
1570	^1,4-dimethyl-3-cyclohexenyl methyl ketone	0.01	
1614	*1-terpinen-4-ol	0.02	
1615	^ <u>myrcenol</u>	0.06	0.05
1615	*3,7-dimethyl-1,5,7-octatrien-3-ol(hotrienol)	0.06	0.19
1635	^ <u>1-p-menthen-9-al</u> (!)	0.03	0.02
1639	^2,3-dimethyl-bicyclo[2,2,1]hept-2-ene (santene A !)	0.03	
1641	^beta-terpineol	0.02	
1660	^ <u>1,3-p-menthadien-7-al</u>	0.13	0.15
1661	*g-terpinene	0.03	
1687	^Z-beta-ocimenol	0.2	0.12
1703	^1,8-menthadien-4-ol	0.01	
1706	^ <u>beta-santalol</u>	0.03	0.02
1713	(-)-alpha-terpineol	0.24	0.12
1717	^g-terpineol(p-menth-4(8)-en-1-ol)	0.03	0.02
1781	^( <u>R)-(+)-beta-citronellol</u>	0.03	0.06
1829	^santene (B !)	0.02	
1853	beta-damascenone	0.1	0.1
1865	geraniol	0.1	0.05
1969	*6-ethyl-2-methyl-delta-1-bicyclo[4.4.0]decen-8-one		0.06
2019	^4-(1-methylethenyl)-1-cyclohexene-1-methanol (perilla alcohol)		0.01
2056	*(+/-)-trans-nerolidol	0.02	0.04
2067	^1-p-menthen-9-al		0.09
2100	^exo-(+-)-1,4,5-trimethyl-9-methylene-bicyclo[3.3.1]nonan-2-one		0.06
2227	^1,4-dimethyl-7-(1-methylethyl)azulene (guaiazulene)		0.01
2327	*farnesol	0.07	0.18
2336	^dihydro-actinidiolide	0.02	
2371	^geranic acid	0.05	
	Compounds of benzene ring		
1243	^p-cymene	0.01	
1317	^1,2,3-trimethylbenzene		0.02
1429	^ <u>p-cymenyl</u>	0.01	0.01
1518	1-chloro-2-methyl-benzene	0.02	1

1529	benzaldehyde	0.04	0.01
1548	^2-ethenyl-1,3,5-trimethyl-benzene (mesitylethylene)	0.01	
1620	*(R*,R*)-(.+)-1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-benzene		0.08
1758	^2-methyl-3-(3,4,5-trimethylphenyl)-2-butene	0.01	
1805	^methyl salicylate	0.01	0.02
1842	*b-phenylethyl acetate	0.43	0.47
1868	^p-cymen-8-ol	0.02	0.03
1880	^2-methoxy-phenol (guaiacol)	0.02	0.02
1895	benzenemethanol	0.18	0.5
1932	benzeneethanol	9.45	11.34
2046	*p-ethylguaiacol		0.01
2127	^1-[6-Hydroxy-2-methyl-3-(1-methylethyl)phenyl]-ethanone		0.06
2167	^eugenol		0.01
2169	^p-ethylphenol		0.04
2172	*o-ethylphenol		0.04
2194	^4-vinyl-2-methoxy-phenol	0.28	0.15
2235	^ <u>1-(2,3,6-trimethylphenyl)-2-butanone</u>	0.02	0.02
2268	ethyl 2-hydroxy-3-phenylpropanoate		0.25
2291	^ <u>1-(2,3,6-trimethylphenyl)-3-buten-2-one</u>	0.07	0.08
2300	^beta-phenylethyl-2-methyl butyrate		0.01
2353	^4-vinylphenol	0.03	0.04
	S-containing compounds		
1534	dihydro-2-methyl-3(2H)-thiophenone	0.04	0.08
1566	*sulfinylbis-methane		0.01
1712	^2-thiophene carboxaldehyde		0.02
1730	3-methylthiopropanol	0.23	0.22
	Acetals		
949	*1-ethoxy-1-methoxy-ethane	0.04	0.02
961	1,1-diethoxyethane	8.19	9.3
999	1,1-diethoxybutane	0.34	0.47
1008	*Acetal-A		0.03
1085	*1-(1-ethoxyethoxy)-pentane	5.3	
1069	*1,1-diethoxy-ethane		0.05
1147	^2-ethoxy-2-methyl-propane		0.02
1286	*2,2'-[ethylidenebis(oxy)]bis-pentane	1.0	0.04
	Alcohols, aldehydes, ketons		
971	* <u>ethanol</u>	0.14	0.06
971	^isovaleraldehyde		0.05
1014	2-butanol	0.11	0.08
1058	*2-methyl-1-propanol	0.37	0.66
1101	* <u>1-butanol</u>	0.04	0.03
1160	^ <u>1-pentanol</u>	0.05	0.2
1168	* <u>3-methyl-1-butanol</u>	31.4	32.28
1205	*1-pentanol		0.01
1206	*3-methyl-3-buten-1-ol		0.01
1253	*3-hydroxy-2-butanone (acetoin)		0.05
1272	*3-(2,2-dimethylpropoxy)- 2-butanol		0.02
1275	*4-methyl-1-pentanol		0.03
1290	*3-methylpentanol		0.06
1319	* <u>1-hexanol</u>	1.15	0.7
1332	* <u>3-hexen-1-ol</u>	0.03	0.03
1357	*trans-3-hexenol	0.06	0.01
1390	*cis-2-hexen-1-ol		0.01
1437	* <u>1-heptanol</u>	0.06	0.04

1500	*(S)-3-ethyl-4-methylpentanol-1		0.04
1554	* <u>n-octanol</u>	0.02	0.03
1668	*nonyl alcohol		0.02
1984	*1-dodecanol		0.03
2348	^1-hexadecanol	0.03	
2510	1-heptadecanol		0.15
	Furans, O-heterocycles		
982	*2,4,5-trimethyl-1,3-dioxolane	0.4	0.17
1452	2-formylfuran	0.7	0.82
1463	*2,5-dimethoxy-3-n-butyl-tetrahydrofuran	0.01	0.04
1502	^ <u>1-(2-furanyl)-ethanone (2-acetylfuran)</u>	0.03	0.06
1580	^ <u>5-methylfufural</u>	0.07	0.04
	N-containing constituents		
1970	1-(2-cyanoethyl)-2-ethyl-4-methylimidazole	0.44	0.1
	Lactones		
1919	cis-3-methyl-4-octanolide(cis-oaklactone)	0.33	
1987	*trans-3-methyl-4-octanolide (trans-oaklactone)	0.04	
2054	gamma-nonalactone	0.08	0.03
2204	delta-decalactone	0.06	0.03
2397	delta-dodecalactone	0.03	
	Indenes		
1988	^2,3-dihydro-3,3,5,7-tetramethyl-1H-inden-1-one	0.08	
1992	^2,3-dihydro-3,3,5,6-tetramethyl-1H-inden-1-one		0.06
2133	2,3-dihydro-3,3,5,6-tetramethyl-1H-inden-1-one	0.38	0.57
	Constituens of naphthalene skeleton		
1762	^6-(1,1-dimethylethyl)-1,2,3,4-tetrahydro-naphthalene	0.02	0.01
1777	3,8,8-trimethildihydronaphthalene	0.19	0.04
1941	1,2,3,4-tetrahydro-1,1,6,8-tetramethyl-naphthalene	0.8	0.02
1761	^3,4-dimethyl-4-hydroxynaphthalen-1(4H)-one		0.02
1777	1,2-dihydro-1,1,6-trimethyl-naphthalene (TDN)		0.17
1942	^2,4-dimethyl-4-hydroxynaphthalen-1(4H)-one		0.41
2028	^1,2,3,4-tetrahydro-4,5,7-trimethyl-1-naphthol		0.02
2070	^1,2-dihydro-3,5,8-trimethyl-naphthalene		0.01
2070	Esters of fatty acids		
959	ethylacetate	2.71	0.17
1017	*acetic acid 2-methylpropyl ester (isobutylacetate)		0.03
1032	*ethyl butanoate	0.56	0.35
1043	*ethyl 2-methylbutyrate	0.50	0.01
1045	*3-methyl-butanoic acid ethyl ester		0.02
1097	*isoamyl acetate	9.13	2.53
1132	*(E)-2-butenoic acid ethyl ester	2.13	0.01
1199	*hexanoic acid ethyl ester (ethyl caproate)	1.9	1.43
1240	* <u>n-hexyl acetate</u>	0.26	0.06
1240 1311	ethyl lactate	0.26	2.8
1311		0.5	0.01
	*methyl octanoate	2.47	
1425	*ethyl octanoate (ethyl caprylate)	2.47	2.53
1514	ethyl 3 hydroxybutyrate	0.06	0.08
1644	butanedioic acid, ethyl methyl ester	1.07	0.08
1655	*ethyl decanoate (ethyl caprate)	1.06	0.92
1679	*isoamyl octanoate		0.02
1691	butanedioic acid diethyl ester (diethyl succinate)	1.56	9.67
1711	*ethyl 9-decenoate	0.06	
1711 1818	ethyl 4-hydroxybutanoate		0.08

1926	ethyl 3-methylbutyl butanedioate	0.15	0.56
2060	*isopropyl myristate	0.02	
2072	*tetradecanoic acid ethyl ester	0.18	0.05
2162	^diethyl 2-hydroxypentanedioate		0.02
2164	*ethyl pentadecanoate	0.01	
2242	*1-methylethyl ester of hexadecanoic acid	0.14	0.1
2254	hexadecanoic acid ethyl ester	0.68	0.17
2267	^ethyl 2-hydroxy-3-phenylpropanoate	0.1	
2277	*ethyl 9-hexadecanoate	0.08	0.06
2422	ethyl stearate	0.12	
2439	(Z)-9-octadecenoic acid ethyl ester	0.16	0.05
2443	*ethyl (E)-oleate		0.03
2476	ethyl linoleate	0.37	0.04
2526	methyl linolenate	0.4	
	Fatty acids		
1489	*acetic acid		0.06
1618	isobutyric acid		0.11
1685	butanoic acid		0.03
1717	*2-methylhexanoic acid		0.33
1722	^2-methyl-butanoic acid (active valeric acid)		0.12
1732	^3-methyl-butanoic acid (delphinic acid)	0.07	
1897	hexanoic acid (caproic acid)	2.0	2.04
2096	octanoic acid (caprylic acid)	4.84	7.41
2298	*decanoic acid (capric acid)	2.02	2.77
2487	*dodecanoic acid	0.28	
	Hydrocarbons		
941	methylcyclohexane	0.48	0.37
2174	*cyclododecane	0.05	
2349	*cyclotetradecane	0.1	0.09
2512	*cyclohexadecane	0.11	

"Area %" values are the averages of 9 determinations (3 independent measurements of each wines with 3 injection of all extracts; n = 3 x 3 for every wines). The standard deviatons are within  $\pm$  10 % in the 0.01- 0.10 area % range;  $\pm$  5.0 - 8.0 % in the 0.10 - 1.5 area % interval; and  $\pm$  3.0 - 5.0 % in the 1.5 - 15.0 area % interval, related to the mean.

[6-Hydroxy-2-methyl-3-(1-methylethyl)phenyl]-ethanone, 0.06 %; 2167, ^eugenol, 0.01 %; 2169, ^p-ethylphenol, 0.04 %; 2172, \*o-ethylphenol, 0.04 %; 2268, ethyl2-hydroxy-3-phenylpropanoate, 0.25 %; 2300, ^beta-phenylethyl-2-methyl butyrate, 0.01 %). The list is dull we must admit, but clearly demonstrates the bad need of the Likens-Nickerson preparation step considering the organo-leptic significance of the majority of the "^signed" (*i.e.* LN-SDE extracted) components.

The case is the same in the "Terpenes, sesquiterpenes and relatives" class as well, where many primary compounds of importance featuring the species character occur only in the LN-SDE extracts. This chemical category deserves some words. Theoretically a bit more fragrant trait of the Szekszárdi Kadarka was expected, due to the better habitat. In fact the analysis shows the opposit. In the wine of the Great Plains 35 primary constituents occur with a ratio of 2.47 %, whilst 31 components of 2.33 % in the Szekszárdi Kadarka merely. The difference seems insignificant, but was detectable sensorically as well. The research fellows of the Department of Enology organised a tasting exam to evaluate the two wines. Unfortunately the analysis prior to the test consumed 4.5 L of both samples and the rest was not enough for an exact sensory panel tasting experiment, barely for an organoleptic one. That is why the sensory evaluation results are missing. In spite of the virtually paltry disparity of the compound numbers and ratio data, studying the referring columns of Tab. 2 the values clearly prove that Kiskörösi Kadarka (of the Great Plains) is reasonably richer in most of the scent impact primary components than the Szekszárdi one.

### Conclusion

A two step sample preparation method elaborated at our Department made us capable of investigating the relative aroma-picture of two high quality Kadarka wines by the primary (terpenes and relatives), secondary (alcohols and other oxigenated substances, esters and fatty acids) and tertiary (mainly the benzene and relatives, lactons, ... etc.) categories separately. The goal of the work was to describe the varietal (*i.e.* cultivated variety characterising) aroma-structures of the samples deriving from famous Hungarian wineries of the two typical Kadarka growing habitats, the Great Plains and Szekszárd. The primary aroma-spectra of the wines disregarding the similarity of a small part in the pictures (circled in the right wing of Fig. 2) differ substantially due to the big quality difference of the terroirs. Our results show that the poor sand soil of the Great Plains yields a Kadarka wine wealthier in terpene and relative compounds than the loess of Szekszárd. The analytical data are supported fairly by the organoleptic experiences.

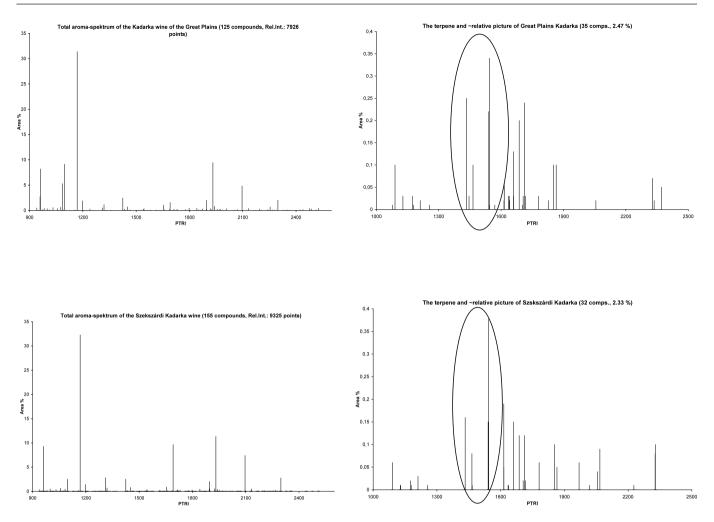
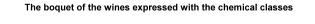


Fig. 2: The total (left side) and the primary aroma-structure (right side) of the two Kadarka wines



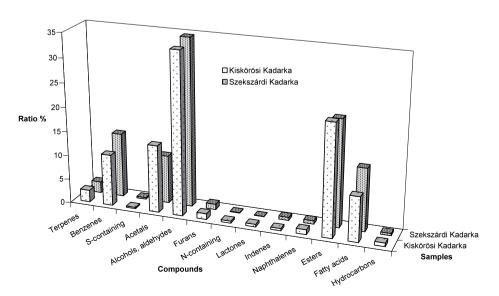


Fig. 3: The "comprehensive" visual representation of the volatile constituents

### References

- BURDOCK, G.A., 2010: Fenaroli's Handbook of Flavor Ingredients. CRC Press Boca Raton, 6<sup>th</sup> Edition.
- EPERJESI, I., KÁLLAY, M., MAGYAR, I., 2003: in "Enology" 4<sup>th</sup> Edition. Mezőgazdasági Kiadó, Budapest (in Hungarian).
- GÓMEZ GARCÍA-CARPINTERO, E., SÁNCHEZ-PALOMO, E., GONZÁLEZ-VIÑAS, M.A., 2011: Aroma characterization of red wines from cv. Bobal grape variety grown in La Mancha region. Food Research International 44, 61-70.
- GÓMEZ GARCÍA-CARPINTERO, E., SÁNCHEZ-PALOMO, E., GÓMEZ-GALLEGO, M.A., GONZÁLEZ-VIÑAS, M.A., 2012: Free and bound volatile compounds as markers of aromatic typicalness of Moravia Dulce, Rojal and Tortosí red wines. Food Chemistry 131, 90-98.
- IVANOVA, V., STEFOVA, M., STAFILOV, T., VOJNOSKI, B., BIRO, I., BUFA, A., KILAR, F., 2012: Validation of a method for analysis of aroma compounds in Red Wine using Liquid-Liquid Extraction and GC-MS. Food Anal. Methods 5, 1427-1434.
- JANYIK, F., 2010: The comparison of Kadarka clones, MSc. Theses, Corvinus University of Budapest (in Hungarian).
- KORÁNY, K., AMTMANN, M., 2005: A practical, theory supported approach of linear temperature programmed gas chromatographic retention indices used in the recognition experiments of Hungarian food specialities, called "Hungarics". J. Food Comp. Anal. 18, 345-357.
- KORÁNY, K., AMTMANN, M., 2006: An experimentally supported, mathematical explanation of the gas chromatographic elution behaviour of the long-chain carbon members of the homologous series. J. Food Comp.

Anal. 19, 813-821.

- KORÁNY, K., MEDNYÁNSZKY, ZS., AMTMANN, M., 2000: Preliminary results of a recognition method visualizing the aroma and fragrance features. Acta Alimentaria 29, 187-198.
- KOVÁCS, T., KÁLLAY, M., KORÁNY, K., 1999: Visualization of the gas chromatography/mass spectrometry data of muscat ottonel must and wine measurements. Int. J. Hort. Sci. 5, 16-21.
- PERESTRELO, R., FERNANDES, A., ALBUQUERQUE, F.F., MARQUES, J.C., CÂMARA, J.S., 2006: Analytical characterization of the aroma of Tinta Negra Mole red wine: Identification of the main odorants compounds. Analytica Chimica Acta 563, 154-164.
- TAKLER, A., 2004: The past and present of Kadarka vine in the Szekszárd terroir, MSc. Theses, Corvinus University of Budapest (in Hungarian).
- ÚJVÁRI, T., 2007: The significance of *Hungaric*-vine species, MSc. Theses, Corvinus University of Budapest (in Hungarian).
- VEVERKA L., JELINKOVA, M., HRON, K., BALIK, J., STAVEK, J., BARTAK, P., 2012: Chemical markers in the aroma profiles of South Moravian red wine distillates. Czech J. Food Sci. 30, 369-376.

### Address of the authors:

Mariann Csóka, Dr. Mária Amtmann and Prof. Kornél Korány, Department of Food Chemistry and Nutrition, Faculty of Food Science, Corvinus University of Budapest, H-1118 Budapest, Hungary

Dr. Diána Ny. Sárdy and Prof. Miklós Kállay, Department of Enology, Faculty of Food Science, Corvinus University of Budapest, H-1118 Budapest, Hungary