Investigation of volatile profile of varietal Gewürztraminer wines using two-dimensional gas chromatography

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Summary
Each varietal wine has its own characteristic aroma profile, which can be described by determination of its volatile organic compounds (VOC) profile. The aim of this work was to characterize Gewürztraminer wine using two-dimensional gas chromatography coupled to time-of-flight mass spectrometry, preceded by solid phase microextraction of volatile compounds from headspace, and identify VOC responsible for typical aroma profile of this varietal wine. In 30 wine samples, in total 288 volatiles were identified, while 153 were found in each studied sample. These common attributes creating varietal fingerprint of Gewürztraminer wine were represented by 50 esters, 28 terpenoids and C_{13}-norisoprenoids, 25 higher alcohols, 23 furans, pyrans and lactones, 13 volatile acids, 10 carbonyl compounds, 3 sulphur compounds and 1 volatile phenol. Differentiation among Gewürztraminer wines and wines of other vine varieties was mainly perceived through the following components: *cis*-rose oxide, sulcatol, *(Z)*-β-ocimene, 4-vinylguaiacol, furan, 2,5-furandicarboxaldehyde, 2(5H)-furanone, solerone, α-angelica lactone, 2-hydroxy-γ-butyrolactone, β-hydroxybutyrolactone, methyl pyruvate and methyl formate. Regardless of vintage and used technology, in all tested Gewürztraminer samples, VOC previously connected only with oak (maltol), botrytization (*p*-cymene), non-saccharomyces activity (blackberry thiophenone), insect pheromones or plants other than *Vitis vinifera* (isogeraniol, β-farnesene, sulcatone, sulcatol, ethyl 3-methylthiopropionate) were identified.

Keywords
Gewürztraminer; wine; volatile organic compounds; two-dimensional gas chromatography

The composition of odour active compounds is one of key parameters that are used to differentiate wines based on their geographical origin, production technology or variety. Specific sensory characteristics of particular wine originate from the presence of certain volatile organic compounds (VOC) that belong to various chemical classes. These compounds occur in different ratios and their concentrations vary within a range from a few micrograms to several hundreds of milligrams per litre. Wine aroma is very complex and develops gradually during the winemaking process. It is influenced by many factors: mostly by vine variety (primary aroma represented by terpenoids, C_{13}-norisoprenoids, C_6-alcohols, aldehydes and noble volatile sulphur compounds), technological processing, especially alcoholic and malolactic fermentation (secondary aroma consisting of higher alcohols, volatile acids, esters, aldehydes, ketones, lactones, volatile sulphur and phenolic compounds), storage conditions and aging (tertiary aroma represented by non-enzymatically created esters, substances extracted from wooden barrels or autolysed yeasts, as well as by degradation and oxidation products of carotenoids and terpenoids) [1–3].

Gewürztraminer is one of the world's oldest vine varieties spread in wine-producing regions of Europe, America and Australia. It offers full bodied wines, which are patterned with heavy rose-like to fruity aroma. VOC profile of Traminers is one of the most complex among all varietal wines and is characterized by high concentrations of terpenoids (β-citronellol, citronellyl acetate, geraniol,

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linalool, nerol, α-terpineol) with typical presence of *cis*- and *trans*-rose oxide [3].

Two-dimensional gas chromatography (GC×GC) together with high data acquisition rate detector (time-of-flight, TOF, mass spectrometer) is one of the most suitable systems for identification and quantification of constituents in complex samples especially regarding trace-level analysis. This technique is convenient especially for comprehensive characterization of wine VOC profile which can often consist of more than 800 compounds. Comparing VOC profiles of wines of one variety with VOC profiles of other varietal wines, compounds typical for the investigated variety can be defined [4].

The aim of this work was to characterize VOC profile of Gewürztraminer wines by GC×GC to identify VOC typical for wines of this unique variety. Results of this study can serve as the source material for future identification of Gewürztraminer among other varietal wines or for works dealing with identification of VOC in wine generally.

MATERIALS AND METHODS

Wine samples

The VOC profile of Gewürztraminer (GT) wines was determined for 30 varietal samples of wines obtained from 22 winemakers from Slovakia. Varietal wines, as they are defined by law of European Commission (EC No. 607/2009 [5]), have to contain at least 85% of wine of one variety. Still wines analysed in this study were 100% GT and classified in all residual sugar-based categories: dry (residual sugars 0–4 $g \cdot l^{-1}$; 20 samples), semidry (4.1–12 $g \cdot l^{-1}$; 4 samples), semisweet (12.1–45 $g \cdot l^{-1}$; 4 samples) and sweet (over 45 $g \cdot l^{-1}$, 2 samples). Studied still GT wines were of following vintages: 2008 (2 samples), 2011 (5 samples), 2012 (10 samples) and 2013 (13 samples). Additionally, 11 non-GT varietal wines of Slovak origin, namely, Moravian Muscat (5 samples), Pinot noir (5 samples) and Riesling (1 sample) were also analysed in order to identify differences in VOC profiles.

Gas chromatography

For sample preparation, 0.5 g NaCl (p.a.; Merck, Darmstadt, Germany) was added into 6 ml of wine mixed with 20 μl of ethanol solution of 1.60 $mg \cdot l^{-1}$ benzophenone (internal standard). VOC were isolated from headspace using solid phase microextraction (SPME; MultiPurpose Sampler, Gerstel, Mülheim an der Ruhr, Germany) by divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 μm fibre (Supelco, Bellefonte, Pennsylvania, USA). SPME fibre was exposed to the headspace for 30 min at 60 °C under continuous stirring at 6.67 Hz. VOC were desorbed from SPME fibre in GC inlet heated at 250 °C in splitless mode kept for 5 min.

For GC×GC analysis, Pegasus IV system (Leco, St. Joseph, Michigan, USA) consisting of Agilent 6890N GC (Agilent Technologies, Palo Alto, California, USA) coupled to a Pegasus III time-of-flight mass spectrometer (TOF/MS) and a dual-stage quad-jet cryogenic modulator (Leco) was used. Column set used for GC×GC analysis consisted of primary highly polar and secondary moderately polar column. Primary column DB-FFAP (Agilent Technologies) with stationary phase nitroterephthalic acid-modified polyethylene glycol had length 30 m, internal diameter (*id*) 0.25 mm and film thickness of stationary phase (d_f) 0.25 μm. Secondary column BPX-50 (SGE, Milton Keynes, United Kingdom) with stationary phase of 50% phenyl polysilphenylene-siloxane had length 1.39 m, *id* 0.10 mm and d_f 0.10 μm. Modulation period was 8 s and modulator offset +30 °C in relation to the primary oven, cold pulses generated using dry N_2 gas cooled by liquid N_2, heated dry air for hot pulses. Following temperature programs were used for separation: for the 1st dimension: initial temperature 40 °C was kept for 10 min, after then ramped with 2 $°C \cdot ml^{-1}$ to the final temperature 220 °C that was kept for 5 min; for the 2nd dimension: initial temperature 50 °C was kept for 10 min, ramped at 2 $°C \cdot ml^{-1}$ to the final temperature 230 °C and held for 5 min. The injector was heated to 250 °C and operated in splitless mode. Helium (99.996% purity, Merck) was used as carrier gas at a constant flow 1 $ml \cdot min^{-1}$. The transfer line was maintained at 240 °C. The temperature of ion source was set at 230 °C, ionization energy of 70 eV was used and detector voltage was set at 1700 V. Vacuum was maintained on the constant value of $1.5 \cdot 10^{-5}$ Pa and ions in the mass range of *m*/*z* 29–400 were acquired at a rate of 100 s^{-1}.

Data processing and analysis

Acquisition control and data processing was performed automatically using ChromaTOF software (version 4.21, Leco). Automated peak find and spectra deconvolution with a baseline offset of 0.8 and signal-to-noise set to value 50 were used for data treatment. Individual peaks were identified by comparison of retention times and mass spectra with standards (when available) and data found in library of National Institute of

Standards and Technology (NIST 14 Mass Spectra library; Scientific Instrument Services, Ringoes, New Jersey, USA). Tentative identification of VOC was performed based on MS comparison with NIST 14 MS library with a minimum match factor 850. For determination of the experimental 1st dimension linear temperature programmed retention index (*LTPRI*) of each compound, a series of *n*-alkanes was analysed under the same conditions. Experimental *LTPRI* values ($LTPRI_{exp}$) were compared with *LTPRI* of standards ($LTPRI_{st}$) and/or with reference *LTPRI* values ($LTPRI_{litr}$) obtained from NIST WebBook Chemie database. A compound was considered as identified if the difference between $LTPRI_{exp}$ and $LTPRI_{st}$ was less than 20 units. In case of missing standards, compounds were considered only tentatively identified based on comparison of $LTPRI_{exp}$ with $LTPRI_{litr}$.

Relative peak areas of VOC identified in wine samples (A_{rel}) were calculated based on Eq. 1 where A_x was peak area of identified VOC and A_{IS} was peak area of internal standard (benzophenone).

$$A_{rel} = \frac{A_x}{A_{IS}} \quad (1)$$

Standards

Standard compounds and *n*-alkanes were purchased from Sigma-Aldrich/Fluka (Steinheim, Germany) in a purity of ≥95 %. Stock solutions of each standard compound were prepared by dilution in solution of methanol (12 % v/v) and tartaric acid (6 $g \cdot l^{-1}$) in MilliQ deionized water (Merck), extracted from headspace and analysed in the same way as wine samples.

Statistical analysis

Experimental values of A_{rel} of all analysed wines (GT and non-GT) were evaluated by the statistical dispersion method ANOVA to calculate Fisher ratios (*FR*) and *p*-values of each analyte. VOC with *FR* higher than 30.00 were subjected to principal component analysis (PCA) to determine which analytes were responsible for the main differences between GT wines and wines of other vine varieties. Both ANOVA and PCA were performed using software Statistica 10 (StatSoft, Tulsa, Oklahoma, USA).

RESULTS AND DISCUSSION

Thirty GT wines were analysed by HS-SPME-GC×GC-TOF/MS in order to comprehensively describe profile of VOC in these varietal wines. Tab. 1 shows VOC identified both tentatively and based on analysis of standard. Relative peak areas were used to describe and compare semi-quantity of each analyte found in wine samples. To get the image of A_{rel} range of VOC identified in tested wines, minimal, maximal and average value of A_{rel} are presented. Relative peak areas of VOC identified in GT wines were statistically compared with A_{rel} of 11 non-GT wines. Fig. 1A and Fig. 1B represent chromatographic records (GC×GC-TOF/MS) of two analysed samples of GT wines (number 18 and 19). PCA was performed after the previous selection of most significant VOC based on Fisher ratio value. Fig. 2A contains a projection of score plot and Fig. 2B loading plot of PCA of VOC profiles of tested wines.

In 30 GT wines, together 288 volatiles were identified (124 based on comparison with standards and 164 tentatively identified). Out of these, 153 compounds were identified in each sample i.e. these compounds were common to all tested wines (Tab. 1). Occurrence of remaining 135 VOC was variable. Common attributes creating VOC profile of GT wine were represented mostly by esters (50), terpenes and C_{13} norisoprenoids (28), higher alcohols (25), furans, pyrans and lactones (23). Minor occurrence was determined for volatile acids (13), carbonyls (10), volatile sulphur compounds (3) and phenols (1).

Terpenoids

In total, 53 VOC belonging to terpenoids and C_{13} norisoprenoids were identified in GT wines, while 28 of them were present in all thirty samples. Terpenoids typical for aroma of roses, citruses or lilac, namely, geraniol, nerol, linalool, β-citronellol, α-terpineol, β-ocimene isomers and *cis*-rose oxide, were identified in all GT wines. Their concentration in grape and wine is known to depend on many factors but, generally, they occur often concurrently because they are biochemically connected [6, 7]. Another common cyclic terpene, limonene, which was identified in all samples, is typical for citruses but occurs also in grapes and wines of different *Vitis vinifer*a varieties [8, 9]. Derivatives of geraniol and nerol, namely, geranic acid, geranyl vinyl ether, *(Z)*-methyl geranate, isogeraniol, ethyl geranate, nerolidol and nerol oxide, and derivates of linalool, namely, linalool oxide and epoxylinalol, were identified in all 30 studied samples, with A_{rel} significantly lower than A_{rel} of their precursors (Tab. 1). Among linalool derivatives, hotrienol is known to play the most important role in primary aroma of Muscat and other aromatic vine varieties. It is characterized by pleasant odour of linden flowers and was detect-

Tab. 1. Volatile organic compounds identified in Gewürztraminer wines.

$LTPRI_{exp}$	$LTPRI_{lib}$	ID	VOC identified	A_{rel}			*FR*	*p*-value	Odour description
				Min.	Max.	Avg			
Terpenoids, C_{13} norisoprenoids									
1172	1180	ST	L-Limonene	0.55	3.83	1.94	3.91	0.06	Sweet, citrus
1219	1237	TI	(*E*)-β-Ocimene	0.31	1.82	1.16	0.04	0.84	Sweet, herbal
1229	1234	TI	(*Z*)-β-Ocimene	0.11	0.90	0.59	50.42	≤ 0.05	Sweet, floral, herbal
1249	1266	ST	*p*-Cymene	0.01	2.37	1.26	0.00	0.95	Woody, citrus, lemon, spicy
1326	1341	TI	Sulcatone	0.01	0.06	0.03	0.27	0.61	Fruity, apple, creamy
1334	1337	ST	*cis*-Rose oxide	0.33	2.06	1.16	35.76	≤ 0.05	Rose, lychee
1444	1460	TI	Cosmene	0.06	0.88	0.42	4.08	0.05	Floral
1463	1479	ST	Nerol oxide	0.01	2.80	1.09	1.05	0.31	Green, vegetative, floral
1455	1451	ST	Sulcatol	0.02	0.15	0.08	44.27	≤ 0.05	Sweet, oily, green, coriander
1457	1451	ST	Linalool oxide	0.11	0.32	0.22	7.38	≤ 0.05	Woody, floral, green
1493	nf	TI	Geranyl vinyl ether	0.81	6.24	3.65	28.29	≤ 0.05	nf
1503	1523	TI	Theaspirane	0.01	0.11	0.06	4.41	≤ 0.05	Woody, cooling, camphoric
1536	1539	ST	Linalool	2.28	6.48	4.34	5.65	≤ 0.05	Citrus, orange, floral, rose
1584	1594	ST	4-Terpinenol	0.08	0.23	0.16	19.65	≤ 0.05	Woody, earthy, clove
1597	1586	ST	Hotrienol	0.20	1.55	0.88	6.37	≤ 0.05	Sweet, fennel, ginger
1643	1640	TI	Ocimenol	0.01	0.13	0.06	1.65	0.21	Fresh, citrus, lime, cologne
1650	1662	TI	β-Farnesene	0.01	0.19	0.09	10.66	≤ 0.05	Woody, green, vegetative
1677	1657	TI	*Z*-Methyl geranate	0.01	1.13	0.52	28.53	≤ 0.05	Waxy, green, fruity, flower
1680	1689	ST	α-Terpineol	1.93	6.75	4.24	0.15	0.70	Pine, lilac, citrus, woody
1759	1762	TI	Ethyl geranate	0.01	3.19	1.52	20.84	≤ 0.05	Woody, rose, green
1729	1727	ST	Epoxylinalool	0.11	0.32	0.22	1.46	0.23	Musty, camphoric
1754	1762	ST	β-Citronellol	0.47	7.56	3.73	20.68	≤ 0.05	Floral, rosy, sweet citrus
1797	1807	ST	Nerol	0.42	5.20	2.91	9.86	≤ 0.05	Fresh, citrus, floral, green
1797	1813	ST	β-Damascenone	0.08	2.51	1.01	17.95	≤ 0.05	Woody, sweet, fruity, floral
1837	1840	ST	Geraniol	0.40	5.05	2.45	15.44	≤ 0.05	Rose
2026	2031	ST	Nerolidol	0.04	0.22	0.13	3.19	0.08	Floral, green, citrus, woody
2328	2315	TI	Geranic acid	0.01	1.09	0.53	18.73	≤ 0.05	Green, woody, greasy, sweet
1840	1820	TI	Isogeraniol	0.07	0.20	0.09	3.04	0.09	nf
Higher alcohols									
1065	1064	ST	1-Propanol	5.71	15.05	9.90	16.31	≤ 0.05	Musty, yeasty, sweet
1105	1100	ST	Isobutanol	5.84	23.97	13.41	12.81	≤ 0.05	Ethereal, winey
1209	1201	ST	Active amyl alcohol	0.30	8.12	3.52	9.69	≤ 0.05	Fermented, yeasty
1215	1213	ST	Isoamyl alcohol	6.20	20.83	13.66	17.92	≤ 0.05	Pungent, fruity, banana
1251	1247	ST	3-Methyl-3-buten-1-ol	0.04	0.12	0.08	21.87	≤ 0.05	Sweet, fruity
1253	1251	ST	1-Pentanol	0.05	0.39	0.18	5.77	≤ 0.05	Fermented, yeasty, winey
1307	1305	ST	Isohexanol	0.18	0.83	0.50	0.57	0.46	Nutty
1313	1313	ST	2-Heptanol	0.09	0.33	0.20	23.08	≤ 0.05	Lemon grass, sweet, green
1348	1351	ST	1-Hexanol	1.84	10.83	6.69	9.87	≤ 0.05	Ethereal, fruity, alcoholic
1358	1355	ST	(*E*)-3-Hexen-1-ol	0.09	1.31	0.72	1.58	0.22	Green, leafy
1375	1373	ST	(*Z*)-3-Hexen-1-ol	0.09	0.61	0.32	24.63	≤ 0.05	Green, grassy, melon rind
1440	1442	ST	1-Octen-3-ol	0.07	0.59	0.33	14.55	≤ 0.05	Earthy, green, oily, fungal
1446	1449	ST	1-Heptanol	0.03	0.71	0.34	16.27	≤ 0.05	Musty, leafy, vegetative
1477	1485	ST	2-Ethylhexanol	0.24	1.14	0.59	1.23	0.27	Citrus, fresh, floral, oily sweet

Tab. 1. *continued*

$LTPRI_{exp}$	$LTPRI_{lib}$	ID	VOC identified	A_{rel}			*FR*	*p*-value	Odour description
				Min.	Max.	Avg			
1506	1510	ST	2-Nonanol	0.10	0.39	0.23	15.18	≤ 0.05	Waxy, green, creamy, orange
1529	1538	ST	2,3-Butanediol	0.02	15.05	6.57	5.85	≤ 0.05	Fruity, creamy, buttery
1545	1548	ST	1-Octanol	0.24	1.58	0.92	9.20	≤ 0.05	Waxy, green, citrus, floral
1647	1654	ST	1-Nonanol	0.04	0.55	0.27	12.38	≤ 0.05	Fresh, fatty, floral, rose, orange
1706	1706	TI	2-Undecanol	0.05	0.77	0.35	0.10	0.75	Fresh, waxy, sarsaparilla
1749	1754	ST	1-Decanol	0.18	0.73	0.45	15.56	≤ 0.05	Fatty, sweet, floral, orange
1843	1840	ST	1-Undecanol	0.03	0.19	0.10	8.82	≤ 0.05	Fresh, waxy, rose, floral, citrus
1863	1869	ST	Benzyl Alcohol	0.15	0.45	0.29	10.74	≤ 0.05	Jasmine, hyacinth
1896	1901	ST	2-Phenylethanol	0.07	16.23	8.32	15.14	≤ 0.05	Sweet, floral, rose, honey, lilac
1349	1334	ST	3-Methyl-1-pentanol	0.01	2.14	0.90	0.40	0.53	Fusel, cognac, wine, fruity
1450	1434	ST	(*Z*)-2-Hexen-1-ol	0.01	0.15	0.08	17.70	≤ 0.05	Fresh, vegetative, slightly fatty
Volatile acids									
1445	1443	ST	Acetic acid	1.19	80.90	36.11	1.35	0.25	Vinegar
1534	1534	ST	Propanoic acid	0.26	0.69	0.44	0.95	0.34	Pungent acidic and dairy-like
1619	1619	ST	Butanoic acid	1.29	3.12	2.22	46.68	≤ 0.05	Sharp, cheesy, buttery
1731	1733	ST	Pentanoic acid	0.01	0.05	0.03	3.70	0.06	Acidic, sharp, cheese-like
1834	1837	ST	Hexanoic acid	1.70	6.27	3.83	7.73	0.01	Sour, fatty, sweat, cheese
1950	1969	ST	2-Ethylhexanoic acid	0.04	0.30	0.17	1.91	0.17	Herbaceous, earthy
1943	1946	ST	Heptanoic acid	0.06	6.77	2.78	12.91	≤ 0.05	Cheesy, waxy, sweaty
2046	2059	ST	Octanoic Acid	0.79	51.09	27.68	1.65	0.21	Fatty, waxy, vegetable, cheesy
2146	2127	ST	Nonanoic acid	0.49	0.82	0.62	27.34	≤ 0.05	Waxy, dirty, cheesy
2254	2251	ST	Decanoic acid	1.25	14.00	7.01	2.20	0.15	Unpleasant, sour, fatty, citrus
2384	2398	ST	Undecanoic acid	0.01	0.73	0.30	0.00	0.99	Waxy, creamy, cheese-like
1640	1660	ST	2-Methylbutanoic acid	0.01	0.99	0.54	23.41	≤ 0.05	Fruity, sweet
1559	1543	ST	Formic acid	0.20	19.94	10.82	20.85	≤ 0.05	Pungent, vinegar
Esters									
782	779	ST	Methyl formate	5.93	74.63	36.41	36.18	≤ 0.05	Fruity, plum
844	828	ST	Ethyl formate	0.01	16.66	6.66	12.59	≤ 0.05	Ethereal, fermented, cognac
904	896	ST	Ethyl acetate	15.24	41.52	29.06	1.30	0.26	Fruity, nail polish
1004	1004	TI	Ethyl 2-methylpropanoate	0.01	1.64	0.88	16.20	≤ 0.05	Sweet, ethereal, fruity, rummy
1036	1029	ST	Isobutyl acetate	0.89	18.19	8.56	4.51	≤ 0.05	Sweet, ethereal, apple, banana
1046	1028	ST	Ethyl butanoate	0.01	40.97	19.61	3.00	0.09	Sweet, fruity, tutti-frutti
1060	1043	ST	Ethyl 2-methylbutanoate	0.31	5.03	1.94	0.02	0.89	Fruity, estery, berry, tropical
1071	1060	ST	Ethyl isovalerate	0.61	2.64	1.61	12.25	≤ 0.05	Sweet, pineapple, apple, orange
1126	1122	ST	Isoamyl acetate	6.25	50.13	28.03	0.05	0.82	Pear, banana (pear drops)
1135	1133	ST	Ethyl pentanoate	0.01	0.19	0.09	9.20	≤ 0.05	Sweet, fruity, pineapple, apple
1164	1161	TI	Ethyl 2-butenoate	0.24	2.80	1.35	4.12	≤ 0.05	Pungent, rum- and cognac-like
1176	1178	ST	Methyl hexanoate	0.18	0.54	0.34	15.66	≤ 0.05	Fruity, pineapple, ether
1203	1217	ST	Methyl pyruvate	0.07	2.00	0.95	33.55	≤ 0.05	nf
1221	1226	ST	Ethyl hexanoate	3.34	38.67	18.34	0.28	0.60	Sweet, fatty, pineapple, banana
1253	1255	ST	Isoamyl butanoate	0.16	1.08	0.58	7.36	≤ 0.05	Fruity, sweet, tropical, tutti-frutti
1258	1270	ST	Hexyl acetate	0.01	15.73	6.92	0.87	0.36	Green, fruity, sweet, fatty, fresh
1291	1294	TI	Ethyl 3-hexenoate	0.01	0.28	0.10	11.70	≤ 0.05	Green, fruity, rummy, brandy

Tab. 1. *continued*

$LTPRI_{exp}$	$LTPRI_{lib}$	ID	VOC identified	A_{rel}			*FR*	*p*-value	Odour description
				Min.	Max.	Avg			
1305	1321	TI	Propyl hexanoate	0.02	0.15	0.08	0.19	0.66	Sweet, fruity, pineapple, tropical
1336	1320	ST	3-Hexen-1-ol acetate	0.01	1.24	0.60	1.12	0.30	Fresh, green, fruity, pear, melon
1320	1337	ST	Ethyl heptanoate	0.18	1.00	0.57	10.61	≤ 0.05	Fruity, pineapple, banana, cognac
1330	1335	TI	Ethyl 2-hexenoate	0.19	0.90	0.58	0.43	0.52	Rum, fruity, green, sweet, juicy
1342	1358	ST	Ethyl lactate	0.01	4.34	2.09	17.28	≤ 0.05	Butter, cream
1376	1356	ST	Isobutyl hexanoate	0.06	0.26	0.17	49.30	≤ 0.05	Sweet, pineapple, green apple
1373	1388	ST	Methyl octanoate	1.81	4.70	3.10	31.14	≤ 0.05	Waxy, green, sweet, orange
1395	1400	TI	Ethyl 2-hydroxybutanoate	0.02	0.70	0.34	0.49	0.49	nf
1427	1427	ST	Ethyl octanoate	1.17	13.11	7.62	0.97	0.33	Tropical fruit, pineapple, apple
1442	1450	TI	Isopentyl hexanoate	0.01	2.36	1.26	23.53	≤ 0.05	Fruity, sweet, pineapple, cheesy
1506	1526	TI	Propyl octanoate	0.11	0.79	0.43	6.16	≤ 0.05	Coconut
1520	1527	ST	Ethyl nonanoate	0.47	4.33	2.17	30.09	≤ 0.05	Fruity, rose, waxy, rum, wine
1531	1515	TI	Ethyl 2-hydroxy-4-methylpentanoate	0.16	1.32	0.63	7.06	≤ 0.05	Fresh blackberry
1538	1551	TI	Isobutyl octanoate	0.06	0.49	0.30	0.26	0.62	Fruity, green, oily, floral
1556	1572	ST	Isoamyl lactate	0.79	3.38	1.99	6.02	≤ 0.05	Fruity, creamy, nutty
1555	1540	TI	Ethyl 3-hydroxybutanoate	0.05	0.35	0.17	11.31	≤ 0.05	Fruity, green, grape, apple skin
1626	1631	TI	Ethyl methyl succinate	0.01	0.27	0.14	10.94	≤ 0.05	nf
1633	1615	ST	Ethyl decanoate	0.64	19.53	8.58	5.57	≤ 0.05	Sweet, waxy, fruity, apple
1645	1648	ST	Isoamyl octanoate	1.19	13.68	6.51	0.01	0.93	Sweet, fatty, pineapple, coconut
1652	1664	ST	Ethyl benzoate	0.01	0.60	0.31	11.73	≤ 0.05	Sweet, cherry, grape
1676	1689	ST	Diethyl succinate	0.11	11.39	5.16	5.58	≤ 0.05	Mild, fruity, cooked apple
1675	1675	TI	Ethyl 9-decenoate	0.14	2.68	1.20	23.11	≤ 0.05	Fruity, fatty
1741	1750	TI	Isobutyl decanoate	0.01	0.06	0.02	12.27	≤ 0.05	Oily, sweet, brandy, apricot
1761	1755	ST	Methyl salicylate	0.06	0.19	0.12	14.30	≤ 0.05	Sweet, wintergreen, phenolic
1800	1820	TI	Ethyl butyl succinate	0.04	0.58	0.28	14.28	≤ 0.05	nf
1792	1791	ST	Ethyl salicylate	0.01	0.05	0.03	6.81	≤ 0.05	Sweet, tutti-frutti, spicy
1799	1810	ST	2-Phenethyl acetate	0.01	11.89	5.64	5.00	≤ 0.05	Sweet, honey, floral rosy
1837	1820	ST	Ethyl dodecanoate	0.01	2.84	1.35	0.00	0.97	Sweet, waxy, soapy, rummy
1847	1864	ST	Isoamyl decanoate	0.10	2.34	1.25	1.13	0.29	Waxy, banana, sweet, green
2031	2048	TI	Diethyl malate	0.10	1.11	0.53	0.21	0.65	Wine, fruity, apple skin
2114	2120	ST	Ethyl cinnamate	0.01	0.08	0.05	16.92	≤ 0.05	Cinnamon
2150	2134	ST	2-Phenylethyl hexanoate	0.01	0.04	0.02	2.08	0.16	Sweet, honey, floral, waxy
2389	2395	TI	Ethyl hydrogen succinate	0.06	2.85	1.21	10.80	≤ 0.05	nf
Carbonyls									
1021	1020	ST	Diacetyl (2,3-butanedione)	0.01	9.50	4.35	12.51	≤ 0.05	Sweet, creamy, buttery, caramel
1086	1068	TI	2,3-Pentanedione	0.01	2.27	1.16	7.02	≤ 0.05	Buttery, nutty, toasted, caramel
1286	1300	ST	Acetoin	0.54	3.37	1.77	20.45	≤ 0.05	Sweet, creamy, milky, fatty
1331	1318	TI	Acetol	0.05	4.64	2.31	23.95	≤ 0.05	Pungent, sweet, caramel
1481	1495	ST	Decanal	0.14	0.44	0.30	23.98	≤ 0.05	Sweet, orange, waxy, citrus rind
1510	1520	ST	Benzaldehyde	0.40	4.23	2.26	6.93	≤ 0.05	Almond

Tab. 1. *continued*

$LTPRI_{exp}$	$LTPRI_{lib}$	ID	VOC identified	A_{rel}			*FR*	*p*-value	Odour description
				Min.	Max.	Avg			
1631	1640	ST	2-Phenylacetaldehyde	0.01	0.18	0.08	12.46	≤ 0.05	Honey, rose, chocolate, earthy
1638	1640	ST	Acetophenone	0.07	0.24	0.15	1.10	0.30	Sweet, marzipan, vanilla
1694	1709	ST	Dodecanal	0.34	0.94	0.62	12.61	≤ 0.05	Soapy, waxy, aldehydic, citrus
1704	1692	TI	2-Dodecanone	0.01	0.19	0.10	1.76	0.19	Fruity, citrus, floral, orange
Volatile phenols									
2185	2192	ST	4-Vinylguaiacol	0.08	0.85	0.51	35.28	≤ 0.05	Woody, cedar, peanut
Volatile sulphur compounds									
1520	1534	TI	Blackberry tiophenone	0.08	0.42	0.25	10.77	≤ 0.05	Sulphur, fruity, berry
1554	1557	TI	Ethyl 3-methylthiopropanoate	0.01	0.09	0.05	9.79	≤ 0.05	Sulphurous, fruity, tomato
1703	1705	TI	Methionol	0.10	0.97	0.50	7.08	≤ 0.05	Sweet, onion, cooked vegetable
Furans, pyrans and lactones									
820	802	TI	Furan	0.01	0.74	0.41	41.50	≤ 0.05	Ethereal
885	876	ST	Sylvan	0.02	1.84	0.88	22.47	≤ 0.05	Ethereal, acetone, chocolate
1221	1235	ST	2-Amylfuran	0.01	0.28	0.14	0.28	0.60	Fruity, green, earthy
1425	1429	TI	α-Angelica lactone	0.05	0.91	0.49	44.67	≤ 0.05	Sweet, creamy, coconut, vanilla
1461	1457	ST	Furfural	0.01	15.61	9.18	0.00	0.97	Sweet, woody, bready, caramel
1497	1501	TI	2-Acetylfuran	0.11	4.52	2.08	26.04	≤ 0.05	Sweet, almond, nutty, toasted
1567	1567	ST	5-Methylfurfural	0.08	2.50	1.21	16.03	≤ 0.05	Sweet, caramel, bready, coffee
1611	1599	TI	Ethyl 2-furoate	0.30	1.31	0.80	12.37	≤ 0.05	Fruity, floral
1616	1617	ST	γ-Butyrolactone	0.52	1.72	1.09	8.71	≤ 0.05	Creamy, fatty
1655	1656	ST	2-Furanmethanol	0.32	7.72	3.55	25.15	≤ 0.05	Sweet, brown caramel, bready
1746	1745	ST	2(5H)-Furanone	0.32	1.86	1.04	45.80	≤ 0.05	Buttery
1898	1912	TI	4-Methyl-5H-furan-2-one	0.01	0.08	0.04	28.25	≤ 0.05	nf
1899	1916	ST	γ-Octalactone	0.01	0.28	0.14	14.25	≤ 0.05	Sweet, creamy, peach, apricot
1959	1967	TI	Maltol	0.01	0.17	0.07	23.66	≤ 0.05	Sweet, caramel, cotton candy
1978	1996	TI	2,5-Furandicarboxaldehyde	0.04	0.17	0.11	93.90	≤ 0.05	nf
1991	nf	TI	Glutaric anhydride	0.14	0.53	0.29	20.70	≤ 0.05	Acidic
2011	2018	ST	γ-Nonalactone	0.02	0.43	0.19	0.51	0.48	Sweet, fatty, creamy, coconut
2090	2096	TI	Solerone	0.02	1.32	0.73	34.41	≤ 0.05	nf
2126	2137	ST	γ-Decalactone	0.03	0.22	0.11	0.06	0.81	Fruity, peach, creamy, sweet
2162	2142	TI	2-Hydroxy-γ-butyrolactone	0.57	4.74	2.69	39.49	≤ 0.05	nf
2254	2266	TI	Hydroxydihydromaltol	0.05	2.11	0.94	18.34	≤ 0.05	nf
2461	2457	TI	β-Hydroxybutyrolactone	0.02	1.36	0.76	35.49	≤ 0.05	nf
2492	2485	TI	5-Hydroxymethylfurfural	0.76	4.29	1.98	42.20	≤ 0.05	Fatty, musty, waxy, caramel

$LTPRI_{exp}$ – experimental value of linear temperature programmed retention index (*LTPRI*); $LTPRI_{lib}$ – reference *LTPRI* value obtained from NIST WebBook Chemie database; ID – identification; VOC – volatile organic compound; ST – VOC confirmed by authentic standard; TI – tentatively identified VOC; A_{rel} – relative peak area of VOC among 30 wine samples; Avg – average A_{rel} of VOC calculated as arithmetic mean of all 30 values; *FR* – Fischer ratio; nf – not found.
FR and *p*-value (ANOVA) were calculated from 30 A_{rel} values of Gewürztraminer and 11 A_{rel} values of non-Gewürztraminer wine samples.

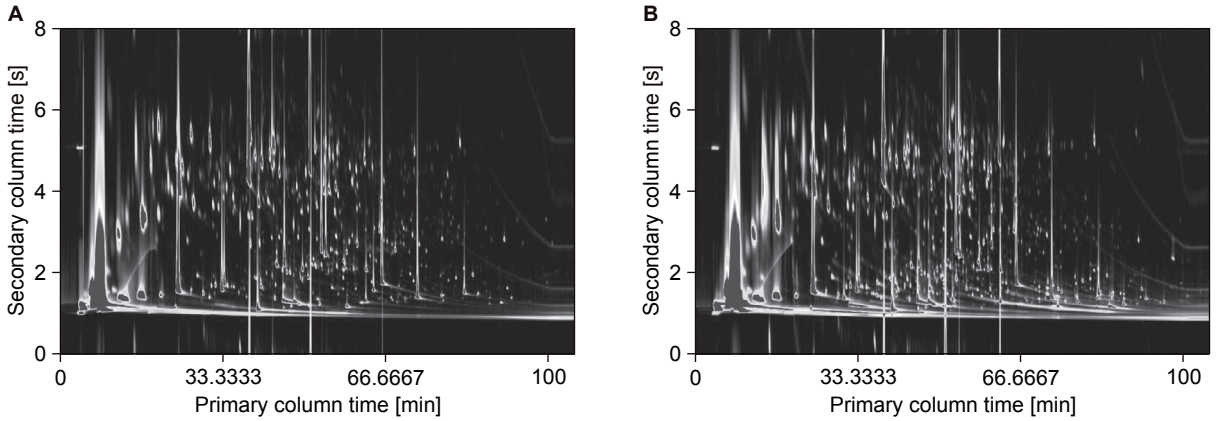

Fig. 1. Chromatographic record (GC × GC-TOF/MS) of Gewürztraminer wine.

A – Sample 18, B – Sample 19.
Primary column: DB-FFAP (Agilent Technologies, Palo Alto, California, USA), secondary column: BPX-50 (SGE, Milton Keynes, United Kingdom).

ed in grapes and wines of Muscat de Alexandria, white Frontignac, GT and Riesling [3, 10]. Isogeraniol was predominantly studied as one of aggregation pheromones of bark beetles [11] and occurs naturally in citruses, wormwood and lychee. From the oenological point of view, it has so far been detected only in grapes of *Vitis vinifera* cv. Fernão-Pires [12].

Sulcatone is a hemiterpenic plant metabolite which is also a part of human odour. It was studied in connection with mosquitoes [13] and found in lemongrass but its presence in wines was not reported yet. *Saccharomyces cerevisiae* and some anaerobic bacteria can reduce sulcatone to sulcatol, which was studied as a population aggregation pheromone in the scolytid beetle [14]. Sulcatol was identified in blackberry, raspberry and apple juice but not in the end products of alcoholic fermentation [15]. Cosmene was first time isolated from flower *Cosmos bipinnatus* and is a part of aroma of laurel tree, hyacinth and *Orchidaceae* family. Its occurrence in grape must or wine was recorded but published and discussed only sporadically. Terpinen-4-ol is considered the main ingredient of tea tree oil and also widespread among the varieties of *Vitis vinifera* [4, 9]. In all tested samples of GT wines, sulcatol, sulcatone, cosmene and terpinen-4-ol were identified.

β-Farnesene is a constituent of various essential oils. This sesquiterpene is released by aphids as kairomone [16] and produced by many plants to repel insects. It is one of terpenoids in hops but its occurrence in grape wine was not wider published. Independently of yeast strain used for the fermentation, it was registered only in grapes and wines of Coda di Volpe variety [17]. In our experiment, β-farnesene was identified in all tested GT samples.

Each studied sample of GT contained C_{13} norisoprenoids theaspirane and β-damascenone. Theaspirane is a component of rose oil and has been found in tea, various fruits including grapes, and also in wines. It is naturally produced by acid-catalysed cyclization of 4-hydroxy-7,8-dihydro-β-ionol and its oxidized products are considered important components of Sauternes wines aroma. β-Damascenone is a degradation product of neoxanthin [18], contributing to varietal aroma of several vine varieties, including Chardonnay, Riesling [19] and Gewürztraminer.

p-Cymene (alkylbenzene related to monoterpene) arises in plants from γ-terpinene and its higher concentration was observed in botrytized wines [20]. None of analysed wines did contain sotolon, a lactone considered the marker of botrytis infection but all of them contained *p*-cymene.

Higher alcohols

The most frequently found fusel alcohols in studied GTs were isoamyl alcohol, isobutanol, 1-propanol, 1-hexanol, 2,3-butanediol and active amyl alcohol. In terms of A_{rel}, dominant position had also 2-phenylethanol and benzyl alcohol, both responsible for intense floral odours. Alcohols with minor abundance were 1-heptanol, 1-octanol, *(E)*-3-hexen-1-ol, *(Z)*-3-hexen-1-ol, 1-octen-3-ol, 2-heptanol, 2-nonanol and 2-undecanol, bringing predominantly green aroma tones, while higher saturated alcohols like 1-nonanol, 1-decanol, 1-undecanol and 2-ethylhexanol are responsible for citrus-like odours. Presence of most fusel alcohols in wine is bound with metabolism of yeast partici-

pating in alcoholic fermentation. Their occurrence and concentration depend on varietal amino acid profile of grapes, metabolic activity of fermenting microflora and technological conditions [21]. Hexanol, octanol and benzyl alcohol are produced primarily in the grape and during fermentation they can be esterified by yeasts [22], thus their occurrence relates more with grapes and primary aroma than with the fermentation process.

Esters

In GT wines, 50 esters common for all 30 analysed samples were identified (Tab. 1). Most frequent were ethyl esters (28), isoamyl (5) and methyl esters (5) and esters derived from acetic (6), hexanoic (6) and octanoic acid (5). Based on average A_{rel} of identified VOCs (Tab. 1), the most abundant esters were methyl formate, ethyl acetate, isoamyl acetate, ethyl butanoate, ethyl hexanoate, ethyl decanoate, isobutyl acetate, ethyl octanoate, hexyl acetate, ethyl formate, isoamyl octanoate, 2-phenylethyl acetate and diethyl succinate.

Esters are very well studied in term of yeast and bacterial metabolism as well as winemaking technology. However, profile of naturally occurring esters in grapes or grape juice is not so widely published. Jackson [19] showed that the major esters in grapes are phenolic esters, methyl antranilate and partially isoamyl acetate in Pinotage. Esters are mostly formed during fermentation and maturation of wine, so they cannot be directly considered as varietal markers of wine. Though, grape juice may contain precursors from which esters are synthesized. Benzyl alcohol and different C_6 and C_8 alcohols are formed primarily in the grape and, during fermentation, they are partially esterified to form acetates or other esters [22]. C_6-, C_8-alcohols and benzyl alcohol were found in all GT samples whereas, among their esters, only hexyl acetate and 3-hexen-1-ol acetate were identified.

Carbonyl compounds

Among all 15 identified aldehydes, only benzaldehyde, dodecanal, decanal and 2-phenylacetaldehyde were present in all 30 GT samples (Tab. 1). 2-Phenyl acetaldehyde is formed by Strecker degradation of phenylalanine and its excessive concentration is typical for oxidized wines and wines stored at higher temperatures [23, 24]. Independently of age and possible oxidation, all analysed GT samples contained this aromatic aldehyde with sweet aroma of honey. Presence of benzaldehyde in wines was firstly connected with epoxy resins and oenological gelatines [25], but later it was confirmed that it occurs also naturally in grapes [26]. However, *S. cerevisiae* is characterized by low production of benzaldehyde, while some non-*Saccharomyces* wine yeasts can produce considerable amounts of it.

Ketones in wine include those originating from grapes (e.g. norisoprenoid ketones, β-damascenone, α-ionone, and β-ionone), ketones produced during alcoholic and malolactic fermentation (diacetyl, acetoin) and ketones formed during aging of wine (acetophenone). Diacetyl, acetol, acetoin, 2,3-pentanedione, acetophenone and 2-dodecanone were identified in all GT samples.

Volatile acids

The major volatile acid present in wine is acetic acid, but other acids such as formic, butanoic and propanoic acid were also previously identified [19, 4]. Studied wines were characteristic by presence of 11 linear aliphatic (C_1–C_{11}) volatile acids and two branched-chain acids, namely, 2-methylbutanoic acid and 2-ethylhexanoic acid.

Lactones, furans and pyrans

Lactones can originate either from grapes or can also be synthesized during fermentation, wine maturation, or be extracted from wood barrels [19]. In terms of their contribution to the aroma of wine, γ-lactones and whiskey lactones play the most important role [27]. In all tested GT wines, γ-butyrolactone, γ-decalactone, γ-nonalactone and γ-octalactone were identified. It was published previously that γ-nonalactone influences also aroma of varietal wines Zinfandel, Pinot Noir, Merlot and Cabernet Sauvignon [28]. Whiskey lactones typical for oaked wines were not identified in any sample of wine. Among other lactones, 2-hydroxy-γ-butyrolactone, β-hydroxybutyrolactone, 4-methyl-5H-furan-2-one and α-angelica lactone were tentatively identified. Less studied lactones, namely, solerone and pantolactone were previously identified in wines submitted to carbonic maceration or oxidative ageing [19, 27]. Pantolactone ($LTPRI_{exp}$ 2020 vs $LTPRI_{st}$ 2023) was identified in 21 out of 30 GT samples, and solerone was identified in all tested wine samples even though wines were treated by none of the mentioned techniques. Sotolon associated with noble rot was not identified in any of 30 GT wines.

Furan derivatives are mostly studied in context of aging of wine in wood [29] but, generally, they can occur also in grape berries, juice, must or wine exposed to elevated temperatures [19]. None of the studied wines aged in barrique so it can be suggested that all identified furanoic compounds originated from grape or were developed during

fermentation or maturation in stainless steel tanks. All GT samples contained 2-acetylfuran, sylvan, furan and 2-amylfuran. From among furfurals, furfural, 5-hydroxymethylfurfural and 5-methylfurfural were identified. Moreover, 2,5-furandicarboxaldehyde, ethyl 2-furoate and 2-furanmethanol were confirmed.

Maltol and its derivatives are breakdown products formed in Maillard reactions and often occur in wines aged in barriques [30, 31]. None of 30 GT samples matured in toasted wooden barrels and, in all of them, hydroxydihydromaltol and maltol were identified. It is possible that these pyrans are generated also during ripening of grape through heating or sunburn of berry skin, which contains cellulose and can undergo Maillard reactions.

Volatile phenols

In GT wines, 16 volatile phenols were identified but only 4-vinylguaiacol was present in all studied samples. 4-Vinylguaiacol originates from the conversion of ferulic acid during fermentation and, together with several terpenes, is considered responsible for spicy character of GT aroma [32].

Volatile sulphur compounds

Three sulphur VOCs, namely, blackberry tiophenone, methionol and ethyl 3-methylthiopropionate were present in all studied samples. Blackberry tiophenone (dihydro-2-methyl-3(2H)-thiophenone) was found previously in mango wine, malt whiskey [33] and in varietal wines of Carménère, Chardonnay, Verdejo and Merlot [34]. It occurs as a metabolic product of different yeast species but only Li et al. [33] linked blackberry thiophenone with *S. cerevisiae*. Ethyl 3-methylthiopropionate was identified in pineapple but also as a varietal contribution of *V. labrusca* cv. Concord grapes [35]. Its occurrence in other grape wines was not published yet. On the contrary, methionol (metabolic product of *S. cerevisiae*) is a very common component of wine VOC profiles.

Multivariate analysis of Gewürztraminer wine volatile compounds

VOCs determined in tested wines, i. e. in 30 samples of GT and in 11 samples of non-GT wines, were analysed using ANOVA and PCA (Fig. 1). Firstly, *p*-values and Fischer ratios (*FR*) were calculated by one-way analysis of variance to determine analytes responsible for the main differences between GT wines and wines of other varieties. *p*-Values lower than 0.05 were reported for 106 of 153 total VOCs, meaning that 106 VOCs showed statistically significant difference for GT and non-GT group means (Tab. 1). This number of variables was too large for a brief PCA analysis, so *FR* values were considered as sorting key. The higher *FR* numerical value obtained for particular compound represented the greater variance between GT and non-GT classes. The correlation matrix was calculated in order to discriminate the

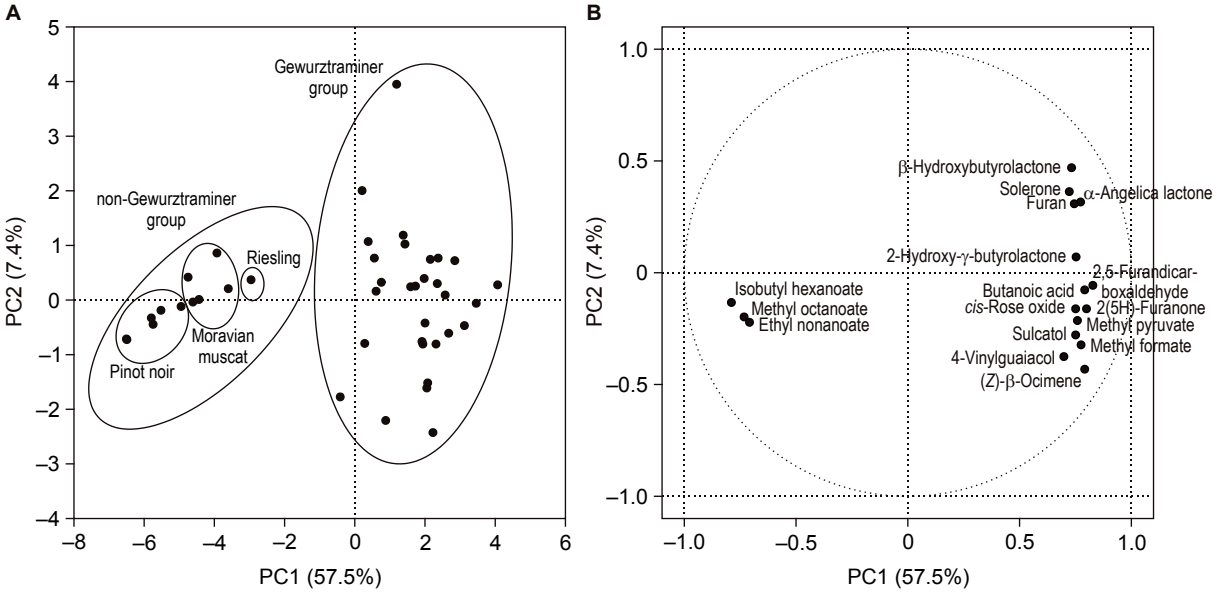

Fig. 2. Principal component analysis of Gewürztraminer wines volatiles.

A – score plot of the first and second principal components; B – loading plot of the first and second principal components.

variables followed by selection of 17 VOCs with *FR* higher than 30.00. PCA explained 64.9% of total variance: 57.5% for PC1 and 7.4% for PC2. As shown in Fig. 1A, PC1 was responsible for differentiation between GT and non-GT wines; PC2 did not contribute considerably and characterized differences among GTs themselves. Fig. 1B shows the corresponding components plot that indicates relative importance of VOC for each class of wine. Comparing the PCA score plot and coordinates of loading plot, VOCs typical for GT wines were identified. *cis*-Rose oxide, which is generally considered the varietal marker of GT wines [36], was identified in all GT wines but also in Riesling and all 5 Moravian Muscat samples. Nevertheless, PCA confirmed very strong positive correlation of PC1 to this terpenoid. Within all terpenoids, sulcatol and *(Z)*-β-ocimene showed the strongest positive correlation to PC1. 4-Vinylguaiacol exhibited the same behaviour as *cis*-rose oxide though its PC1 coordinate was lower. From among furans, 2,5-furandicarboxaldehyde, 2(5H)-furanone, furan and solerone and, among lactones, α-angelica lactone, 2-hydroxy-γ-butyrolactone and β-hydroxybutyrolactone differentiated GT and non-GT wines. Within 50 identified esters, only 32 had *p*-values lower than 0.05 and only 5 esters had *FR* value higher than 30.00. From among these, only methyl pyruvate and methyl formate showed positive correlation to PC1. Very strong positive PC1 correlation was determined for butanoic acid.

CONCLUSION

In this study, analysis of VOCs of 30 Gewürztraminer wines by HS-SPME-GC×GC-TOF/MS is reported. The use of the progressive analytical method allowed us to identify VOCs that are common for all alcoholic beverages as well compounds detected in GT and also in wine generally for the first time. In all GT wines, 288 VOCs were identified, while 153 of them were present in each sample. Results of this study may be valuable for future works dealing with identification of VOCs in wine but also on identification of Gewürztraminer wines among other varieties.

PCA allowed differentiating Gewürztraminer and non-Gewürztraminer samples. Wines of GT variety were characterized dominantly by presence of *cis*-rose oxide, sulcatol, *(Z)*-β-ocimene, 4-vinylguaiacol, furan, 2,5-furandicarboxaldehyde, 2(5H)-furanone, solerone, α-angelica lactone, 2-hydroxy-γ-butyrolactone and β-hydroxybutyrolactone. From among esters, only methyl pyruvate and methyl formate distinguished this variety from the others.

Regardless of vintage, saccharinity of grapes, winemaking technology and used yeast strain, in all tested Gewürztraminer samples VOCs previously connected with using of barriques (maltol), oxidation of wine (2-phenylacetaldehyde), botrytization (*p*-cymene) or with activity of yeasts species other than *S. cerevisiae* (blackberry thiophenone) were identified. VOC profile of Gewürztraminer wines also included compounds found and discussed previously only in connection with insects or plants other than *V. vinifera* (isogeraniol, β-farnesene, sulcatone, sulcatol, ethyl 3-methylthiopropionate).

Acknowledgment

This work was supported by Slovak Research and Development Agency under the contract APVV-15-0333 and by Grant Agency of Ministry of Education of Slovak Republic under the contracts VEGA 1/0573/14 and VEGA 1/0560/14.

The authors would like to thank to Katarína Makyšová and Matúš Hornáček for their valuable co-operation by sample collecting and carrying out a part of sample treatment procedure.

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Received 28 October 2016; 1st revised 4 January 2017; accepted 9 January 2017; published online 14 February 2017..