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Authenticity Assessment of the "Onisiówka" *Nalewka* Liqueurs Using Two-Dimensional Gas Chromatography and Sensory Evaluation

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Abstract The "Onisiówka" *nalewka* liqueur is a regional Polish alcoholic beverage, which is inscribed on the list of regional and traditional products of the Ministry of Agriculture and Rural Development in Poland. It is produced from multiflower honey, black elderberry flower syrup, and spirit. Due to fact that the "Onisiówka" *nalewka* liqueur has never been investigated, these studies are the foundation for further work on this regional alcoholic beverage. The main aim of this work is the authenticity assessment of the "Onisiówka" *nalewka* liqueurs by means of qualitative characteristics of volatile fraction and sensory evaluation. Tentative identification has been performed using two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS). Application of GC×GC-TOFMS allowed for detection of around 350 compounds present in the volatile fraction of the "Onisiówka" from which 102 compounds were tentatively identified. PCA results showed that the first two principal components constitute 96.98% of total variance. Statistical analysis was used to visualize relations between tentatively identified compounds; therefore, it has been demonstrated that 23 chemical compounds may have significant influence on the overall flavor and taste of the "Onisiówka". These substances belong to four chemical classes, in which the greatest number is represented by esters (13), aldehydes (6), alcohols (3), and one terpene compound. According to the sensory evaluation, the Onisiówka is characterized by sweet, honey, fruity, flowery, bitter, and spirituous flavor and taste.

Keywords Onisiówka · Nalewka · Liqueur · GC×GC-TOFMS · Sensory evaluation · Authenticity test

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Introduction

Liqueurs constitute important group of spirit beverages on the global market, which are representing a wide range of traditional drinks (Christoph and Bauer-Christoph 2006). According to the Regulation of the European Union, they are spirit drinks produced by flavoring ethyl alcohol or distillate of agricultural origin by foodstuff such as fruit, herbs, wine, or other agricultural products and sweetened (Regulation [EC] No. 110/2008). The minimum content of alcohol is 15% *v*/*v*, and most frequently, liqueurs are colored by adding agricultural food products, such as caramel and honey. The most popular liqueurs are made of cherries, citrus, herbs, apples, and blackcurrants (Christoph and Bauer-Christoph 2006; Śliwińska et al. 2015). Generally, these beverages are used as aperitif and are served in small glasses after the meal (Egea et al. 2015).

In the scientific literature, there are information about the analysis of liqueurs made from cherry (Ieri et al. 2012; Śliwińska et al. 2016a; Senica et al. 2016), apple (Śliwińska et al. 2016b), lemon (Schipilliti et al. 2013; Naviglio et al. 2015; Naviglio et al. 2016), melon (Hernández Gómez et al. 2009), pineapple (Oliveira et al. 2015), herb (Vázquez-Araújo et al. 2013), and walnut (Stampar et al. 2006; Jakopic et al. 2007). Most studies of these beverages are conducted using chromatography, sensory evaluation, and recently electronic sensing. Among all chromatographic techniques most often

used for identifying volatile fraction of alcoholic beverages is one-dimensional gas chromatography (GC) (Śliwińska et al. 2015). Despite the fact that relatively long time GC analysis allows for separation of around several hundred substances in single run, one-dimensional retention mechanism usually is not enough to prevent co-elution phenomena (Welke and Alcaraz Zini 2011; Cordero et al. 2015). Therefore, more and more often, two-dimensional gas chromatography (GC×GC) is used to analyze alcoholic beverages. The GC×GC-time-of-flight mass spectrometry (TOFMS) technique has found application in wine (Weldegergis et al. 2011; Welke et al. 2012; Samykanno et al. 2013; Bordiga et al. 2013), cachaça (Cardeal et al. 2008; Cardeal and Marriott 2009; Capobiango et al. 2013), and selected spirit beverages (such as vodka, whisky, tequila) (Cardeal and Marriott 2009), also fruit spirit (Villière et al. 2012; Capobiango 2015), Japanese sake (Takahashi et al. 2016), and Chinese liqueur (Zhu et al. 2007; Yao et al. 2015) analysis.

The variety of liqueurs depends primarily on the geographical origin and climatic conditions of the region in which they are produced. Consequently, this affects the choice of ingredients for the production of liqueurs. In order to protect the traditional and specific for a particular region food products, they are labeled as "Protected Destination of Origin" (PDO), "Protected Geographical Indication" (PGI), and "Traditional Specialty Guaranteed" (TSG), all in accordance with guidelines of the European Union (Śliwińska et al. 2016c). To the group of geographical indications of liqueurs by EU belong, among others, Liquore di limone di Sorrento (Italy), Licor de hierbas de Galicia (Spain), Ratafia de Champagne (France), and Berliner Kümmel (Germany) [Regulation [EC] No. 110/2008; EU Agricultural Product Quality Policy]. Year after year, the list of traditional products designated by the EU is growing. Consequently, analytical techniques are used for authenticity tests, quality control, and adulteration assessment of foodstuff (Borràs et al. 2015). For this reason, the GC×GC-TOFMS instrument is increasingly applied in analysis of regional food products certified by EU commission in terms of profiling, fingerprinting, and traceability of origin. This approach has already been included in studies that concerned hazelnuts (Tonda gentile romana) (Cordero et al. 2008), honeys (Corsican honey) (Cajka et al. 2009; Stanimirova et al. 2010), and olive oils (Monti Iblei, Dauno Gargano) (Magagna et al. 2016).

One of the traditional Polish alcoholic beverages unspecified by the EU is the "Onisiówka" *nalewka* liqueur. However, this drink, since 2006, was inscribed on the list of regional and traditional products of the Ministry of Agriculture and Rural Development in Poland (Traditional Polish Products). Food products located on this list are of high quality and originate from specific regions and characterize by the traditional method of their production dating back at least 25 years (Journal of Laws No. 10/2005, item 68). The "Onisiówka" *nalewka* liqueur is manufactured according to familial recipe, almost 40 years of tradition. The origin of this beverage is closely connected with the farmhouse "Pasieka Wędrowna Barć" located in the village Krzemienica in Pomeranian Voivodeship. Precisely from this region come all the ingredients needed to prepare the "Onisiówka" *nalewka* liqueur such as multiflower honey, black elderberry flower syrup called "hyczka", and spirit. All components are combined without any processing (heating, distillation) in order not to destroy the natural flavors of all ingredients ("Wędrowna Barć"). The final content of alcohol is around 40% *v*/*v* (Traditional Polish Products). According to Śliwińska et al. (2016a), this beverage may be labeled *nalewka*, because it is prepared exclusively in homemade conditions. In addition, the main ingredient of this beverage is honey; therefore, the "Onisiówka" *nalewka* liqueur should not be confused with mead, which is produced by yeast alcoholic fermentation of diluted honey (Pereira et al. 2014, 2015; Dobrowolska-Iwanek 2015).

It is possible to find information about the analysis of volatile fraction of the main ingredients of the "Onisiówka" such as honey (Pontes et al. 2007; Rivellino et al. 2013), black elderberry fruits (Ochmian et al. 2010; Vítová et al. 2015), and flowers (Kaack and Christensen 2008). However, the "Onisiówka" *nalewka* liqueurs have never been investigated. For that reason, knowledge about this regional and traditional beverage should be increased. The main aim of this work is the authenticity assessment of the Onisiówka nalewka liqueurs by means of qualitative characteristics of volatile fraction and sensory evaluation. Tentative identification has been performed by GC×GC-TOFMS, and statistical analysis was made using Principal Component Analysis (PCA).

Materials and Methods

Samples, Chemicals, and Materials

Five bottles of the "Onisiówka" *nalewka* liqueurs were acquired from original producer, Agroturism Farm "Pasieka Wędrowna Barć" (Krzemienica, Poland) in Pomeranian Voivodeship in 2014. Figure 1 presents original bottle and label of this beverage. Tightly sealed and secured bottles of beverages were stored in below room temperature in the dark place prior to analysis.

A C7–C30 alkane mixture for linear retention index (linear temperature programmed retention index (LTPRI)) calculations was from Sigma-Aldrich (St. Louis, MO, USA).

Sample Preparation

Samples for GC×GC-TOFMS analysis were prepared in the proportion of 2 ml of liqueur "Onisiówka" and 4 ml of deionized water and then transferred into 20-ml glass vials (Śliwińska

Fig. 1 Original bottle of 250 ml and label of "Onisiówka" *nalewka* liqueur

et al. 2016d). All samples were sealed with magnetic screw caps closing with 1.3-mm-thick PTFE/silicone septum purchased from Sigma-Aldrich (Poznań, Poland). High-purity deionized water used for diluting liqueurs was obtained from a MilliQ A10 Gradient/Elix System (Millipore, USA). During the research ten repetitions were performed for each sample.

Samples for sensory evaluation contained 20 ml of "Onisiówka" *nalewka* liqueur.

Headspace Generation

The headspace generation for GC×GC-TOFMS procedure was preceded by headspace solid-phase microextraction (HS-SPME) extraction. A Gerstel autosampler (MPS autosampler, Gerstel, Mülheim, Germany) with agitator and SPME fiber conditioning station was used to extract the volatile compounds from liqueurs. The SPME fiber with divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS, thickness of 50/30 μm, length of 1 cm) coating (Sigma-Aldrich, Munich, Germany) was used. Prior to GC×GC-TOFMS analysis, the fiber was conditioned according to the instructions provided by the producer. Before the extraction, the samples were kept at 40 °C for 5 min. During the extraction, the vial was agitated at 700 rpm. Extraction was carried out at 40 °C for 20 min. After the extraction, the fiber was removed from the vial and transferred to the injector of a gas chromatograph for thermal desorption of the analytes at 250 °C for 5 min (Śliwińska et al. 2016a).

Instrumentation

The GC×GC system consisting of an Agilent 7890A equipped with liquid nitrogen-based quad-jet cryogenic modulator and a split/splitless injector, and Pegasus 4D TOFMS (LECO Corp., St. Joseph, MI, USA) was used for analysis. The first dimensional nonpolar column was 30 m × 0.25 mm i.d. × 0.25 μm film thickness Equity-1 (Supelco, Bellefonte, PA, USA). The second dimensional polar column was 2 m × 0.1 mm i.d. × 0.1 μm film thickness SolGel-Wax (SGE Analytical Science, Austin, TX, USA).

The injector, transfer line, and ion source temperature was set at 250 °C. The separation was performed using the following temperature program for the primary oven: initial temperature 40 °C, kept for 3.5 min, ramped at 7 °C/min to 250 °C, and held for 5 min. The secondary oven temperature was programmed from 45 °C, kept for 3.5 min, ramped at 7 °C/min to 255 °C, and held for 2 min (Śliwińska et al. 2016a). The modulation period was 6 s. Hydrogen (N6.0 class) was used as a carrier gas at a flow rate at 1.0 ml/min. The transfer line was at 250 °C, and the ion source set was 250 °C. The detector voltage was 1600 V. Mass spectra were collected from *m/z* 40–400 at ten spectra per second. The acquisition delay was 460 s.

Sensory Evaluation

The sensory evaluation of the "Onisiówka" *nalewka* liqueur was performed using the point method (PN-64/A-04022). The number of ten panelists, comprising five women and five men, evaluated the flavor, taste, and color of each beverage according to a five-point scale (1—bad to 5—very good). All persons were selected to preliminary test of taste and small according to procedure (PN-A-79529-2:2005). Additionally, panelists were asked to describe the color and the most perceptible flavors and tastes. The panel tasting took place in an air-conditioned room (21 °C). The "Onisiówka" *nalewka* liqueur samples were evaluated in triple repetitions.

Data Processing

Analysis of the data obtained by the use of the GC×GC-TOFMS system was done using the algorithm for peak deconvolution with a baseline offset of 0.5 and signal to noise (S/N) set up at 100. The ChromaTOF software (LECO Corp., version 4.24) was used for this purpose. Tentative identification of volatile compounds in the "Onisiówka" *nalewka* liqueurs was obtained by comparing experimental LTPRIs with literature retention indices for first dimension GC (Welke et al. 2014a). Retention data of a series of *n*-alkane mixture, under

the same experimental conditions, employed for the chromatographic analysis of beverage volatile fraction used for experimental LTPRI. These LTPRI values were calculated using Van den Dool and Kratz equation (Van Den Dool and Kratz 1963). Literature LTPRI values were obtained for 100% dimethyl polysiloxane capilary GC columns. Mass spectrometric information of each chromatographic peak was compared with NIST 2011 library considering with minimum similarity value of 85%. Whenever a LTPRI was not found in the scientific literature to match with the experimentally determined LTPRI or chemical compounds contain less than six carbon atoms, only then manual assess, with respect to the mass spectra match and the unique mass, was used for quantification.

Statistical Analysis

Statistical analysis was performed using GC×GC-TOFMS dataset consisting average values of peak areas, heights, and S/N ratio of 102 chemical compounds (taken from the ChromaTOF software), and data achieved after sensory evaluation consisting of all points of sensory assessment obtained by panelist group.

The statistical analysis was performed by using The Unscrambler v9.7 (CAMO Software AS, Oslo, Norway). A nonsupervised multivariate method, the PCA was used for visualization of relations between tentative identified compounds in the "Onisiówka" *nalewka* liqueur obtained using GC×GC-TOFMS. Results obtained from sensory evaluation were analyzed by using Microsoft Excel 2007 software. All figures were performed by using OriginPro 8.3 software (Northampton, MA, USA).

Results and Discussion

GC×GC-TOFMS Analysis

More than 350 compounds detected in each sample of the "Onisiówka" *nalewka* liqueur by GC×GC-TOFMS; 102 were tentatively identified with the following criteria: time of first dimension (1D) was set at 650 s, which was calculated on the basis of alkane mixtures, minimum of mass spectral similarity value set at 85%, S/N ratio set at 100, and the comparison of experimental and literature LTPRIs. Figure 2 shows a color plot obtained after HS-SPME/GC×GC-TOFMS analysis of the "Onisiówka" *nalewka* liqueur.

The threshold value of similarity parameter was established at 850 (which means the 85% similarity of experimental mass spectrum with the mass spectrum taken from the database of NIST 2011). Values below mentioned threshold and signal-to-noise ratio were not taken into consideration during further data analysis. Regarding Fig. 3, the identification method of chemical compound, for example, nonanal, based on database of mass spectrum, was explained.

The number of chromatographic peaks found resulted by S/N ratio established in this study (over 100). LTPRI experimental values were calculated according to the Van den Dool and Kratz equation (Van Den Dool and Kratz 1963). Additionally, values of LTPRI for compounds containing six atoms of carbon (C6) were extrapolated. The values of LTPRI were also compared with literature LTPRI for every compound. The acceptance criteria were less than 15 units of difference between experimental and literature LTPRI. Due to these requirements, 102 volatile compounds were tentatively identified in the Onisiówka nalewka liqueurs (Table 1).

Among 102 tentatively identified compounds present in the volatile fraction of the "Onisiówka" *nalewka* liqueurs by GC×GC-TOFMS, esters were present in highest numbers (32), followed by aldehydes (21), terpenes (18), ketones (10), alcohols (11), acid (1), and others (9), which includes alkanes (1), furans (2), nitriles (1), and aromatic hydrocarbons (5). Percentage distribution of chemical classes present in the volatile fraction of the "Onisiówka" *nalewka* liqueurs was shown in Fig. 4.

The greatest group by number of identified chemical compounds was esters. Esters were also characterized by the highest contribution in the volatile fraction of this beverage (Fig. 4). These compounds have major impact on the aroma profile of alcoholic beverages, and they influence flavor of final product. Generally, esters are mostly formed from estrification of fatty acids with alcohols during fermentation process (Christoph and Bauer-Christoph 2006). Ester content in alcoholic beverages is also affected by maceration process and sensory properties of ingredients such as fruits or herbs used for production. For this reason, a large amount of esters are identified in various alcohol beverages made from fruits, such as fruit spirits, wines, cognacs, and liqueurs (Nikićević et al. 2011; Welke et al. 2014b; Śliwińska et al. 2015). In general, esters of lower carboxylic acid and lower alcohols characterized with fruity sensory properties, for example, butyl acetate, ethyl pentanoate, ethyl hexanoate, hexyl acetate, ethyl 2-hydroxypropanoate, and ethyl octanoate. However, fatty acid esters like ethyl hexadecanoate contribute to waxy flavor (Jørgensen et al. 2000). Aldehydes, ketones, and alcohol are other large chemical groups of identified chemical compounds in the "Onisiówka". According to Jørgensen et al. (2000) and Cajka et al. (2007) aldehydes, ketones, and alcohol represented major chemical groups of honey and elder flower volatile compounds. Most of them characterized fruity and floral flavor such as 3-methylbutanol, benzyl alcohol, 2-ethylhexanol, 1-octanol, 1-nonanol, hexanal, octanal, benzeneacetaldehyde, nonanal, 2-phenylpropenal, 2,4-nonadienal, decanal, 2-decenal, dodecanal, butylphenyl methylpropional, (E)-3-penten-2-one, 2-heptanone, 6-methyl-5-hepten-2-one, acetophenone, 2-nonanone, 4-methylacetophenone, 2-decanone, 2-undecanone, 2-

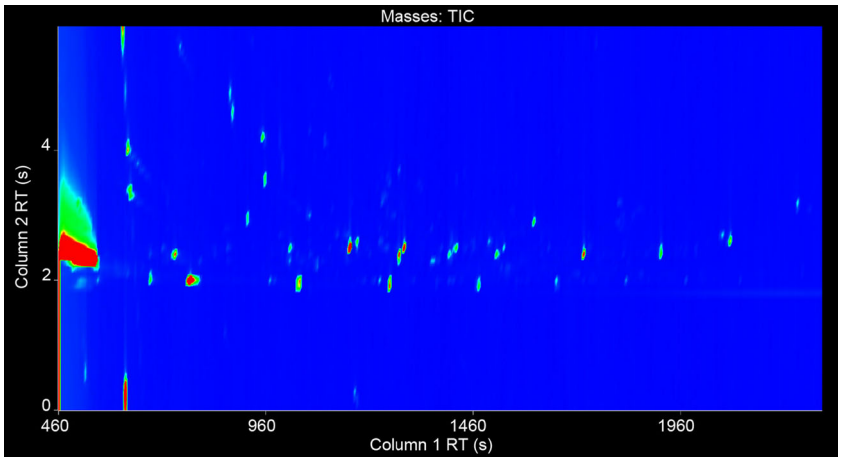

Fig. 2 Separation of volatiles of the "Onisiówka" *nalewka* liqueur isolated by the use of HS-SPME technique. Presented color plot of GC×GC-TOFMS chromatogram was made in mode of total ion mode current (TIC)

dodecanone, and 2-pentadecanone. Most of these compounds were previously identified in several studies of honey, elderberry fruits, and flowers (Jørgensen et al. 2000; Baroni et al. 2006; Pontes et al. 2007; Kaack 2008; Kaack and Christensen 2008;

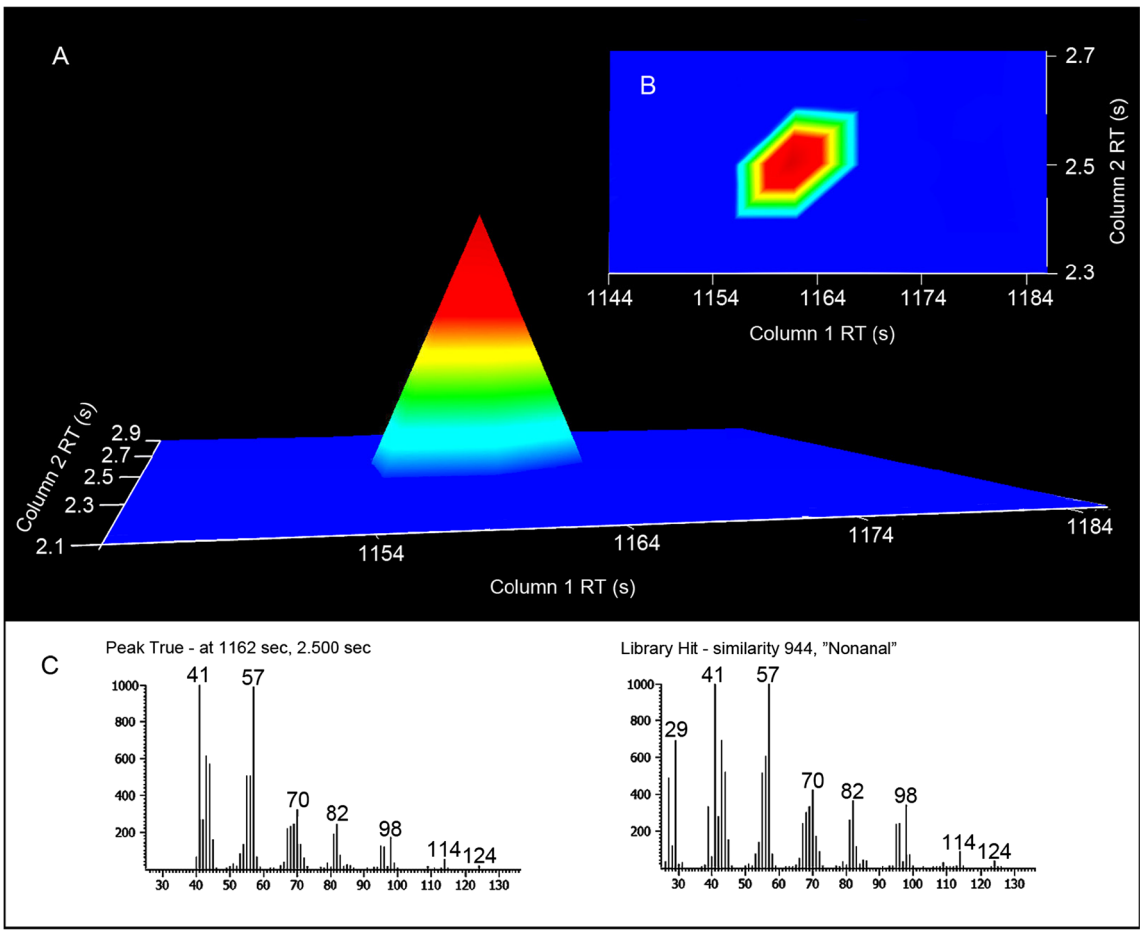

Fig. 3 The example of tentatively identified nonanal extracted by the use of HS-SPME from the "Onisiówka" *nalewka* liqueur and analyzed through the GC×GC-TOFMS system. Identification was done on the basis of comparison of experimental data with the mass spectrum included in the database of NIST 2011. **a**, **b** Enlarged fragment of the region of color plot (3D) obtained using $m/z = 57$. **c** Experimental mass spectra of the compound and the respective mass spectra of the same substance included in NIST 2011 library

Table 1 The identification of compounds from the volatile fraction of the "Onisiówka" *nalewka* liqueur using HS-SPME/GC×GC-TOFMS

Name	Chemical formula	S.	U. mass	$LTPRI_{Exp}$	$LTPRI_{Lit}$	Sensory description	I. n.
Alcohols							
3-Methylbutanol[a]	$C_5H_{12}O$	910.8	55	–	–	Alcoholic, balsamic, bitter, burnt, cheese, fermented, fruity	1
1-Hexanol[b]	$C_6H_{14}O$	926.7	56	850[f]	847.9	Floral, fruity, green, herbaceous, sweet	90
3-Hexen-1-ol[b]	$C_6H_{12}O$	931.4	67	842.3	837	Fresh, green	9
1-Heptanol	$C_7H_{10}O$	915.2	70	960	951.8	Fresh, light green, nutty	13
Benzyl alcohol	C_7H_8O	907.6	79	1020	1022	Aromatic, floral, fruity, sweet	15
2-Phenylethanol	$C_8H_{10}O$	958.6	91	1092	1084	Floral, honey, lilac, rose, spice	92
1-Octen-3-ol	$C_8H_{16}O$	840.2	57	972	965	Carrot, herbaceous, spicy	20
2-Ethylhexanol	$C_8H_{18}O$	930.2	57	1020	1013	Citrus, green, rose,	25
1-Octanol	$C_8H_{18}O$	944.6	56	1056	1057	Fatty, floral, green, herbaceous	30
1-Nonanol	$C_9H_{20}O$	892.4	56	1144	1151	Fatty, floral, fruity, green	42
1-Dodecanol	$C_{12}H_{26}O$	942.8	69	1450	1457.1	Fatty, waxy	74
Aldehydes							
2-Furancarboxaldehyde (furfural)[a]	$C_5H_4O_2$	945.8	95	–	–	Almond, bread, sweet	8
2-Methyl-2-butenal[a]	C_5H_8O	917.6	84	–	–	Cacao, coffee	3
Hexanal[b]	$C_6H_{12}O$	942.6	57	780.8	777	Acorn, fruity, grassy, herbaceous, leafy	5
Benzaldehyde	C_7H_6O	974	106	944	935	Almond, burnt sugar, fruity, woody	12
2-Hydroxybenzaldehyde	$C_7H_6O_2$	921.8	122	1024	1024	Medicinal	16
Octanal	$C_8H_{16}O$	937.2	57	988	984	Citrus, fatty, floral, fruity	22
Benzeneacetaldehyde	C_8H_8O	955.2	91	1020	1010	Floral, grassy, green, rose, sweet	26
3-Octenal	$C_8H_{14}O$	900.6	70	1040	1031	Nf	27
2-Methylbenzaldehyde	C_8H_8O	931.4	91	1048	1038	Nf	29
3-Methylbenzaldehyde	C_8H_8O	931.4	91	1048	1057	Nf	93
4-Methylbenzaldehyde	C_8H_8O	882.8	91	1060	1064	Floral, fruity, mild, spicy, sweet	32
4-Methoxybenzaldehyde	$C_8H_8O_2$	931	135	1204	1211	Anise, minty, sweet	36
Nonanal	$C_9H_{18}O$	945.6	57	1084	1083	Citrus, floral, fruity, lavender, melon	39
2-Phenylpropenal	C_9H_8O	928.4	103	1131	1150	Nf	40
4-Ethylbenzaldehyde	$C_9H_{10}O$	876.4	134	1148	Nf	Nf	43
2,4-Nonadienal	$C_9H_{14}O$	849.4	81	1176	1165	Watermelon	45
Decanal	$C_{10}H_{20}O$	959.8	57	1187	1184	Burnt, fatty, floral, green, lemon, orange peel	61
2-Decenal	$C_{10}H_{18}O$	912.2	70	1234.8	1237	Fatty, orange	63
2,4-Decadienal	$C_{10}H_{16}O$	860.4	81	1282.6	1290	Fatty	64
Dodecanal	$C_{12}H_{24}O$	951.6	57	1390	1385	Citrus, fatty, herbaceous, lily, oily, waxy	76
Butylphenyl methylpropional	$C_{14}H_{20}O$	850.6	189	1511.1	1500	Floral	80
Ketones							
(E)-3-Penten-2-one[a]	C_5H_8O	928.8	69	–	–	Fruity	2
2-Heptanone	$C_7H_{14}O$	893.6	58	876	864	Cheese, fruity, nutty	10
6-Methyl-5-hepten-2-one	$C_8H_{14}O$	903	43	972	973	Blackcurrant, boiled fruit, citrus, pepper, woody	19
Acetophenone	C_8H_8O	966.2	105	1044	1043	Almond, cheese, floral, musty, sweet	28
2-Nonanone	$C_9H_{18}O$	885.2	58	1072	1073	Baked, fatty, fruity, green	37
4-Methylacetophenone	$C_9H_{10}O$	931.2	119	1152	1157	Almond, floral, hay, sweet	44
2-Decanone	$C_{10}H_{20}O$	924.6	58	1177.3	1175	Citrus, floral, orange	65
2-Undecanone	$C_{11}H_{22}O$	918	58	1272.7	1274	Fresh, fruity, green, musty, orange	67
2-Dodecanone	$C_{12}H_{24}O$	850.8	58	1375	1377	Citrus	77
2-Pentadecanone	$C_{15}H_{30}O$	878.2	58	1687.5	1688	Floral, herbaceous, spicy	84
Acids							

Table 1 (continued)

Name	Chemical formula	S.	U. mass	$LTPRI_{Exp}$	$LTPRI_{Lit}$	Sensory description	I. n.
Octanoic acid	$C_8H_{16}O_2$	868.4	60	1160	1158	Cheese, fatty acid	35
Esters							
Ethyl 2-hydroxypropanoate[a]	$C_5H_{10}O_3$	925	45	–	–	Ethereal buttery, fruity	7
Ethyl 2-methylpropanoate[b]	$C_6H_{12}O_2$	913.6	71	750	742	Nf	4
Butyl acetate[b]	$C_6H_{12}O_2$	888.6	43	788.5	791	Banana, bitter, fruity, green, pear, pineapple, sweet	6
Ethyl pentanoate	$C_7H_{14}O_2$	864.4	88	888	890	Fruity, grassy, green, minty, orange	11
Ethyl furoate	$C_7H_8O_3$	913.2	95	1028	1029	Floral, plum	17
Ethyl hexanoate	$C_8H_{16}O_2$	900.8	88	988	980	Anise, apple, fruity, strawberry, sweet	21
Hexyl acetate	$C_8H_{16}O_2$	951.6	43	1000	987	Citrus, fruity, green, herbaceous, spicy	24
Ethyl diethoxyacetate	$C_8H_{16}O_4$	850.6	47	1060	Nf	Nf	31
Methyl benzoate	$C_8H_8O_2$	904.4	105	1071	1061.4	Floral, herbaceous, honey, watermelon, sweet	33
Diethyl butanedioate	$C_8H_{14}O_4$	968.6	101	1136	1136	Floral, fruity, potato, watermelon	34
Ethyl heptanoate	$C_9H_{18}O_2$	910	88	1080	1081	Fruity	38
Ethyl benzoate	$C_9H_{10}O_2$	953.6	105	1140	1138.2	Camomile, fruity, minty, lavender, melon	41
Ethyl 2-hydroxybenzoate	$C_9H_{10}O_3$	894.2	120	1128	1236.8	Floral, minty, sweet, wintergreen	46
Hexyl butanoate	$C_{10}H_{20}O_2$	852.8	89	1179.9	1173	Apple, fruity, green	59
Ethyl octanoate	$C_{10}H_{20}O_2$	929.6	88	1178.3	1173	Anise, floral, fresh, fruity, green, metholic, sweet	60
Ethyl benzeneacetate	$C_{10}H_{12}O_2$	951.4	91	1213	1218	Anise, cinnamon, floral, fruity, sweet, waxy	62
Ethyl nonanoate	$C_{11}H_{22}O_2$	911.6	88	1272.7	1279	Waxy	66
Ethyl 3-phenylpropionate	$C_{11}H_{14}O_2$	911.2	104	1318.2	1320	Floral, pleasant, sweet	68
4-tert-Butylcyclohexyl acetate	$C_{12}H_{22}O_2$	911.8	57	1360	1346	Balsamic	71
Ethyl decanoate	$C_{12}H_{24}O_2$	931.8	88	1375	1379	Fruity, grape, waxy	72
2-Propenyl 3-cyclohexylpropanoate	$C_{12}H_{20}O_2$	845.2	55	1405	1407	Fruity	73
Pentyl 2-hydroxybenzoate	$C_{12}H_{16}O_3$	858	120	1540	1543	Nf	75
Ethyl undecanoate	$C_{13}H_{26}O_2$	890.6	88	1473.7	1477	Nf	78
Hexyl salicylate	$C_{13}H_{18}O_3$	914.2	120	1636.8	1652	Balsamic, floral, hay, herbaceous, waxy	79
Ethyl dodecanoate	$C_{14}H_{28}O_2$	938.6	101	1572.2	1577	Leafy, mango, waxy	81
Benzyl benzoate	$C_{14}H_{12}O_2$	895	105	1716.7	1726	Balsamic, herbaceous, oil	82
Ethyl tridecanoate	$C_{15}H_{30}O_2$	896.6	88	1681.3	1677	Nf	83
Ethyl tetradecanoate	$C_{16}H_{32}O_2$	935.4	101	1764.7	1778	Etheral, oily, waxy	85
Diisobutyl phthalate	$C_{16}H_{22}O_4$	895.4	149	1811.8	1819	Nf	86
Isopropyl myristate	$C_{17}H_{34}O_2$	887.2	60	1807.143	1827	Floral, oily fatty	87
Ethyl pentadecanoate	$C_{17}H_{34}O_2$	939.6	88	1878.571	1877	Fruity, grassy, green, minty, orange, yeast	88
Ethyl hexadecanoate	$C_{18}H_{36}O_2$	928.2	88	1978.571	1978	Mild sweet, waxy	89
Terpenes							
α-Pinene	$C_{10}H_{16}$	863	93	939.1	932	Camphor, citrus, fruity, green, pine, woody	47
α-Myrcene	C_10H_{16}	914	93	986.9	983	Balsamic, fruity, lemon, spicy, sweet	48
Limonene	$C_{10}H_{16}$	938.4	68	1034.8	1025	Citrus, fruity, minty, orange, peely	49
1,8-Cineole	$C_{10}H_{18}O$	861.2	71	1034.8	1033	Camphor, herbaceous, mentholic, minty, sweet	50
(Z)-Linalool oxide (furan)	$C_{10}H_{18}O_2$	926.6	59	1069.6	1070	Rose, wood	51
p-Cymene	$C_{10}H_{12}$	941.2	117	1086.9	1079	Balsamic, citrus, fruity, herbaceous, lemon, spicy	52
Terpinolene	$C_{10}H_{16}$	923.4	93	1091.3	1089	Fruity, herbaceous, pine, sweet, woody	53

Table 1 (continued)

Name	Chemical formula	S.	U. mass	$LTPRI_{Exp}$	$LTPRI_{Lit}$	Sensory description	I. n.
Hotrienol	$C_{10}H_{16}O$	855.4	71	1095.5	1085	Fungal	95
Nerol oxide	$C_{10}H_{16}O$	919.2	68	1143.5	1144	Floral, green, oily, spicy	54
Terpinen-4-ol	$C_{10}H_{18}O$	858.8	93	1177.3	1172	Fruity, herbaceous, licorice, musty, spicy, sweet, terpenic, woody	96
α-Terpineol	$C_{10}H_{18}O$	897.8	59	1186.3	1183	Anise, floral, fruity, minty, oily, peach	97
Borneol	$C_{10}H_{18}O$	854.6	95	1165.2	1155	Balsamic, camphor, musty	56
(Z)-Rose oxide	$C_{10}H_{18}O$	892.6	139	1104.3	1093	Green	102
Menthol	$C_{10}H_{20}O$	942.6	71	1169.6	1173	Peppermint, mentholic	57
Gardenol	$C_{10}H_{12}O_2$	865	104	1169.6	1165	Sweet	58
Neryl acetate	$C_{12}H_{20}O_2$	864.6	93	1345	1343	Floral, fruity, raspberry, rose	98
Bornyl acetate	$C_{12}H_{20}O_2$	890.6	93	1284	1276	Balsamic, camphor, herbaceous, pine	70
β-Damascenone	$C_{13}H_{18}O$	854	121	1378.9	1371	Apple, fruity, honey, sweet, tobacco	100
Others							
Phenol[b]	C_6HO	951	94	961.5	961	Medicinal, phenolic	101
Benzonitrile	C_7H_5N	910.8	103	960	956	Bitter almond, cherry	14
Toluene	C_7H_8	902.5	91	748	748	Caramelized, etheral, fruity, pungent	91
Benzofuran	C_8H_6O	905.6	118	988	968	Nf	23
1,2-Dimethylbenzene	C_8H_{10}	932.8	91	868	871	Futty, oily, pungent	18
2-Pentylfuran	$C_9H_{14}O$	851.3	81	984	980	Butter, fruity, green bean	94
1-Ethyl-3,5-dimethylbenzene	$C_{10}H_{14}$	866.4	119	1152.2	1050	Nf	55
Dodecane	$C_{12}H_{26}$	918.4	57	1205	1200	Alkane, fusel	69
1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN)	$C_{13}H_{18}O$	851.3	157	1355.9	1336	Licorice	99

Similarity (*S.*): average of similarity of the mass spectrum of the "Onisiówka" volatile compounds with the spectra of standard compounds in NIST 2011. Unique mass (*U. mass*): the most unique ion selected using ChromaTOF data analysis software. Experimental linear temperature programmed retention index ($LTPRI_{Exp}$) calculated using alkane mixtures and nonpolar stationary phase (100% dimethyl polysiloxane). Literature LTPRI ($LTPRI_{Lit}$) on nonpolar stationary phase (100% dimethyl polysiloxane). Sensory description: the classification of olfactory sensation caused by certain chemical compound, which was described in (AroChemBase library). Identification number (*I. n.*): identification number of compound in PCA analysis. Not found (*Nf*): value of LTPRI and sensory description in the literature were not found. Identification of compound was based only on mass spectra from the NIST 2011

[a] Compounds contain less than C6. Identification was based only in mass spectra from the NIST 2011

[b] Extrapolated LTPRI for compounds with contain only C6 below the lower of alkane mixtures analyzed

Ochmian et al. 2010; Rivellino et al. 2013; Dymerski et al. 2013; Vítová et al. 2015). Benzaldehyde and benzenealdehyde have been reported as usual components of unifloral honey (Baroni et al. 2006). Also, benzaldehyde previously has been detected as the most abundant aromatic compound in headspace of elderberry flower drink (Jørgensen et al. 2000). Benzyl alcohol and 2-phenylethanol have been identified and described as contributors to the flavor of elderberry (Mikova et al. 1984). Terpenes are another chemical compound group, which have influence on sensory properties of fruit spirit beverages and liqueurs (Christoph and Bauer-Christoph 2006; Winterová et al. 2008). In this study, 18 terpenes were identified; most of them may affect the pleasant fruity and herbaceous flavor of the "Onisiówka". Terpenes such as (Z)-rose oxide, nerol oxide, and hotrienol are responsible for the characteristic floral aroma of elder flowers (Farkas et al. 1995; Jørgensen et al. 2000). In addition, other identified terpenes such as α-terpineol, terpinen-4-ol, terpinolene, nerol oxide, (Z)-linalool oxide, limonene, and 1,8-cineole have been also detected previously in honeys, elderberry fruits, and flowers (Jørgensen et al. 2000; Jensen et al. 2001; Cajka et al. 2007). There are several compounds which have been reported as common compounds of various honeys, such as toluene, furan, furfural, and hotrienol (Pontes et al. 2007). In the literature, there is information that phenol was identified in different samples of honey (Dymerski et al. 2013). Compounds such as β-damascone, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), and 6-methyl-5-hepten-2-one have been also identified as contributor to elderberry flavors (Poll and Lewis 1986). Full sensory descriptions of all tentatively identified compounds in volatile fraction of the "Onisiówka" *nalewka* liqueur are, according to (AroChemBase library), described in Table 1. It may be noted that most of tentatively identified compounds originate from two main ingredients of this beverage: honey and elderberry flowers. It has been

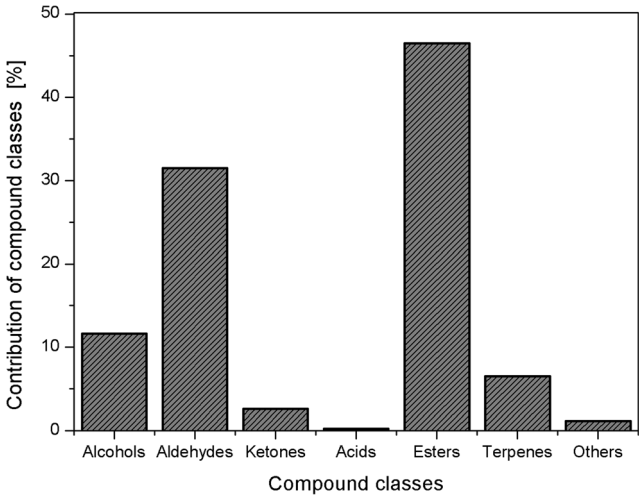

Fig. 4 Percentage contribution of chemical classes present in volatile fraction of the "Onisiówka" *nalewka* liqueur determined by the use of GC×GC-TOFMS

previously reported that honey and black elderberry flowers demonstrate antioxidant and health benefit properties (Malika et al. 2005; Thole et al. 2006; Charlebois 2007; Bertoncelj et al. 2007; Alzahrani et al. 2012; Sidor and Gramza-Michałowska 2015). It may be assumed that the "Onisiówka" *nalewka* liqueur has a positive impact on health.

In order to visualize the relations between tentative identified compounds (102) in the volatile fractions of the "Onisiówka" *nalewka* liqueurs, PCA analysis was performed (Fig. 5). For this statistical analysis, area, height, and signal-to-noise ratio of peak of each compound were used. PCA results showed that the first two principal components accounted for 96.98% of

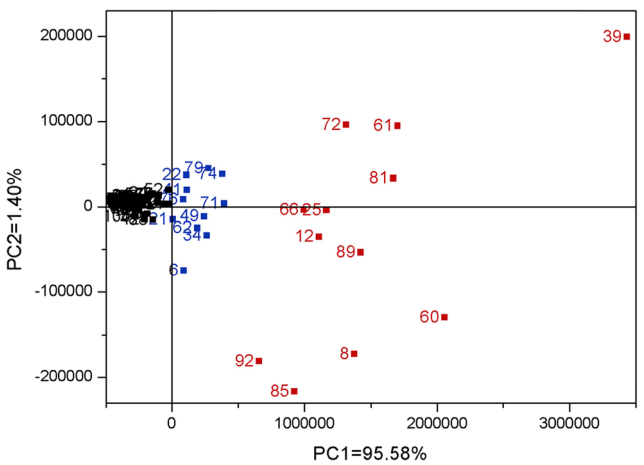

Fig. 5 PCA score plot corresponding to visualize the relations between tentative identified compounds of the "Onisiówka" *nalewka* liqueur using GC×GC-TOFMS

total variance. In II and III quarts, there are 79 compounds in the negative area of PC1. These compounds could not be separated; they are located in a large cluster. It means that the values of used variables are similar compared to all tentatively identified compounds present in the volatile fraction of the "Onisiówka" *nalewka* liqueurs. On the other hand, 23 compounds are located in I and IV quarts in the positive region of PC1. These compounds may be defined. Also, as observed in Fig. 5, these compounds are located in two groups. The first group is located between 0 and 500,000 value of PC1 (in Fig. 5, highlighted in blue color). This group includes the following compounds: octanal, ethyl benzoate, dodecanal, hexyl salicylate, 1-dodecanol, 4-tert-butylcyclohexyl acetate, limonene, ethyl benzeneacetate, butyl acetate, diethyl butanedioate, and ethyl hexanoate. The second group (in Fig. 5, highlighted in red color) is located in a wider range of PC1 from 500,000 to 3,600,000 and includes ethyl decanoate, ethyl nonanoate, 2-ethylhexanol, benzaldehyde, ethyl tetradecanoate, decanal, ethyl dodecanoate, 2-phenylethanol, ethyl hexadecanoate, 2-furancarboxaldehyde, ethyl octanoate, and nonanal. The PCA has shown that these groups of compounds may significantly influence the overall flavor and taste of the "Onisiówka".

Sensory Evaluation

During sensory evaluation of the "Onisiówka" samples, panelist group evaluated color, flavor, and taste according to five-point scale, from 1 (bad) to 5 (very good). Results of this analysis were collected in Table 2. Additionally, panelists were asked to describe the color and the most perceptible flavors and tastes.

According to the panelist group, color assessment of the "Onisiówka" received average score of 2.75, and they described it like honey, lemon chiffon, or straw. In addition, each member of the panelist group observed that evaluated samples had sediment. That color assessment of the Onisiówka may be due to occurring of natural sediment in this beverage, which can detract from the visual appearance of the product (Cernivec 2013). However, according to the panelist group, the "Onisiówka" received higher scores for flavor and taste assessments. Most of them also showed that they sensed sweet, honey, fruity, flower, and bitterness flavor. These sensory properties of the

Table 2 Sensory assessment of the "Onisiówka" *nalewka* liqueurs according to five-point scale

Sensory assessment of the "Onisiówka"		
Color	Flavor	Taste
2.75 ± 1.04	3.88 ± 0.64	3.88 ± 0.64

All given values were presented as arithmetic mean including standard deviation. Sensory evaluation carried out by the application of point method according to PN-64/A-04022

"Onisiówka" originate from several tentatively indentified compounds inter alia 2-phenylethanol, decanal, ethyl octanoate, butyl acetate, ethyl hexanoate, and nonanal. It should be noted that the last mentioned compounds were presented in PCA (Fig. 5) score as chemical compounds characterized by the highest value of peak area, height, and signal-to-noise ratio. Probably, the bitterness of "Onisiówka" originated from used black elderberry flower syrup. All members of the panelist group noticed that spirituous flavor felt very intense. This is due to the use of spirit rather than vodka which has less alcohol content.

Conclusion

In this work, it has been reported for the first time the authenticity assessment of Polish regional beverage, the "Onisiówka" *nalewka* liqueurs, using qualitative characteristics of volatile fraction and sensory evaluation. The comprehensive approach has shown that GC×GC not only represents high separation power but also can further examine the complexity of investigated samples thanks both to the higher level of information achievable from the two-dimensional GC×GC separation and to the possibility of the use of reliable data for chemometric interpretation. This is also made possible by its high sensitivity, which extends identification prospects by taking into account minor components of samples. This study has emphasized advantages of a comprehensive and multidisciplinary approach to interpret the increased level of information that GC×GC separation can provide in selected purposes. Thus, the application of GC×GC-TOFMS has allowed for tentative identification of 102 chemical compounds from around 350 substances detected in volatile fraction of these beverages. Percentage contribution of chemical classes in volatile fraction is presented by esters (46.45%), aldehydes (31.48%), alcohols (11.61%), terpenes (6.52%), ketones (2.57%), one carboxylic acid (0.21%), and others (1.17%), which includes alkanes, furans, nitriles, and aromatic hydrocarbons. Multiflower honey, black elderflower syrup, and spirit are used for the production of the "Onisiówka" *nalewka* liqueur. Most of the tentatively identified chemical compounds originate from the abovementioned matrices. These molecular entities include benzaldehyde, octanal, 2-ethylhexanol, 2-phenylethanol, nonanal, 6-methyl-5-hepten-2-one, nerol oxide, and limonene. The majority of the tentative identified esters, aldehydes, alcohols, and ketones characterize fruity, floral, and green flavor of these beverages. Additionally, PCA statistical analysis was useful to visualize relations between the tentatively identified chemical compounds. The first two principal components constitute 96.98% of total variance, and it has demonstrated that 23 tentatively identified compounds may have significant influence on the overall flavor and taste of this liqueur. In sensory evaluation, the panelist group has assessed flavor and taste of this beverage as sweet, honey, fruity, flowery, bitter, and spirituous. The obtained results of sensory analysis are consistent with the fact of using certain ingredients utilized for production of this beverage. The natural sediment in the "Onisiówka" could be potentially an evidence confirming the use of natural products, such as honey and black elderflower syrup, in its production. The use of these ingredients may also be the reason of some medical properties of this liqueur. Due to the fact that the "Onisiówka" *nalewka* liqueurs have never been investigated, these studies are the foundation for further work on this regional alcoholic beverage. This research allows for dissemination of regional products and probably in the near future can constitute a supplementary material for documents concerning protection of this traditional product in compliance with guidelines of the European Union and apply for the list of the protection of geographical indications of spirit beverages.

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Compliance with Ethical Standards

Conflict of Interest Magdalena Śliwińska declares that she has no conflict of interest. Paulina Wiśniewska declares that she has no conflict of interest. Tomasz Dymerski declares that he has no conflict of interest. Waldemar Wardencki declares that he has no conflict of interest. Jacek Namieśnik declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

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