PECULIARITIES OF AROMATIC COMPOSITION OF THREE WINES MADE FROM WHITE GRAPE VARIETIES SELECTED IN MOLDOVA

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INTRODUCERE

Wine is one of the most complex alcoholic beverages, and its aroma substances are responsible for much of this complexity. Wine flavor can be classified into three groups: varietal, fermentative and wine ageing aroma. Describing the aroma of wines is not a simple task for researchers, because more than 800 aroma compounds such as alcohols, esters organic acids, aldehydes, ethers, ketones and terpenes, etc., have been identified in them, with a wide concentration range varying between hundreds of mg/L to the μg/L or ng/L levels, and their combinations form the character of wine and differentiates one wine from another [1].

The gas chromatography-olfactometry (GC-O) is an analytical method that combines the gas chromatography and sensory evaluation, using the human nose to assess odor components. The human nose has odor detection limit of about 10^{-19} moles [2], therefore GC-O is an extremely valuable and sensitive tool for odor detection.

1. THEORETICAL ISSUES

Chromatography is a method used to decompose complex mixtures of chemicals into their constituents. In essence, the method entails the forced transfer of chemical components along an adsorptive or dissolvent material, which usually is packed in a column or which constitutes the inner lining of a column.

A better estimation of each component's contribution to the aroma may be obtained by sensory evaluation of the separated constituents. Thus, by replacing the flame ionization detector (FID) with a sufficiently large panel of subjects that sniff the effluents of the gas chromatograph with the purpose to detect and characterize the odor-active chemicals.

After injection, the content of the sample is separated by the chromatographic column. Before leaving the column (figure 1), the effluent is divided into two parts: the smallest is directed to the instrumental detector, usually a FID; the largest part is directed to a smelling device (sniffing port) placed at the evaluator's nose height. This method provides simultaneously two signals: the chromatogram of the extract and the recording of odor events perceived by assessors [3].

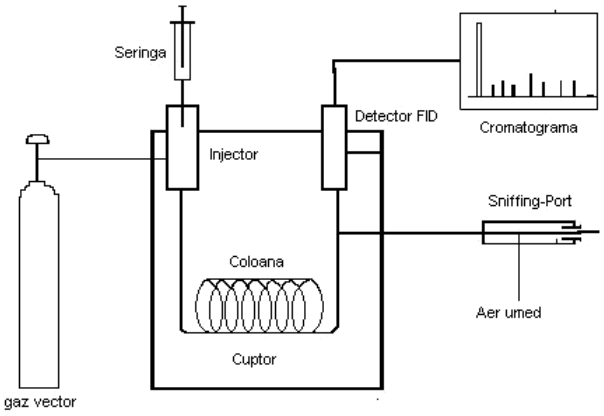

Figure 1. The operating principle of GC-O

Each assessor must perceive the beginning and the end of the flavor and describe it. The individual aromagrams are summed, yielding the global aromagram where frequency of detection is represented in dependence on time or retention index. The olfactometric indices can be used for ranking odorant areas according to their olfactory impact [4].

The odorant areas obtained via GC-O are characterized by three parameters: olfactometric index, average linear retention index (LRI) or LRI interval and flavor descriptors. All this information is used later in the identification of compounds [5].

2. MATERIAL AND METHOD

For analysis were used wines made from Moldavian local grape varieties: Startovyi, Hibernal and Muscat of Ialoveni (harvest 2010) produced at the Practical Scientific Institute of Horticulture and Food Technology from Chişinău.

In order extract aromatic compounds was used the dichloromethane extraction, based on the method proposed by Moio [6].

The olfactometric analysis was performed on 3 extracts by 7 assessors selected in advance and informed that they will analyze three white wines, but no other detail has been specified. The extracts were analyzed by the participants in a different and balanced sequence. The total length of a session was 45 minutes. After injection of the solution into chromatograph column, in order to avoid inhalation of the solvent, the assessor was asked to wait 5 minutes before approaching the nose to the sniffing port (figure 2).

Figure 2. Sniffing-port (with the glass mold of the nose), button and microphone for recording.

The gas chromatograph Hewlett-Packard 5890 was equipped with split/splitless injector and DB-1701 capillary column. Simultaneous processing of both signals was performed using EZchrom Elite (Agilent Technologies) and AcquiSniff ® (© INRA).

Linear retention indices (LRI) of chromatographic peaks and odorant events were calculated using a daily injection of a solution of 13 n-alkanes (from C_7 to C_{19}), analyzed under the same chromatographic conditions as the extracts.

The results of each individual data processing were presented in Excel tables where the LRI peak, the assessor codes, the extract codes and their respective descriptors were indicated. Therefore, 21 tables with olfactometric data were obtained, that subsequently were submitted to mathematical processing. Mathematical processing of olfactometric data was performed using Matlab ® (The Mathwork Inc.), which implements an iterative mathematical function to get a table that contains the number of detections for each tandem wine/odorant area.

3. RESULTS AND DISCUSSIONS

Initially the wines were submitted to sensory analysis sessions. Though considerable dispersion of responses, it was achieved conclusive data and a diagram of sensory profile. The intensity of wine aroma was appreciated with values within a range from 62.5 to 75 pts out of 100.

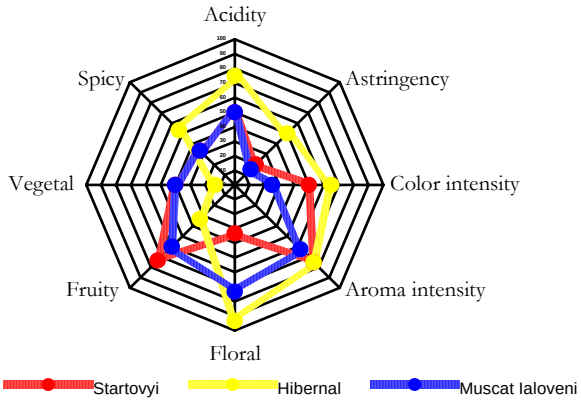

Figure 3. Sensorial profile of studied wines.

On the axes of radar type diagram (figure 3) are set the values and the sensory characteristics for each wine. Descriptors are presented according to the free expression of assessors (table 1).

Table 1. Descriptors set out by the assessors.

The wine	Types of aromas			
	Floral	***Fruity***	***Vegetal***	***Spicy***
Startovyi	Honey	Pear, lemon	Freshly cut hay	Pepper, coconut
Hibernal	Basil, thyme	Pomelo, grapefruit	Grass	Laurel, paprika
Muscat Ialoveni	Acacia flowers	Citrus, pineapple	Celery	Nutmeg

The olfactometric study, using frequency detection, generated 21 individual aromagrams. The number of odorant events related to each wine is situated between 228 (Muscat of Ialoveni) and 238 (Hibernal), meaning that for three wines, seven assessors had spotted 697 events (table 2).

Table 2. Global data of olfactometric analysis.

The wine	***Total odor events***	***Total descript.***	***Events without descript.***	***% Events without descript.***
Startovyi	231	259	22	8,5 %
Hibernal	238	272	26	9,5 %
Muscat Ialoveni	228	250	31	12,4 %
Sum 3 wines	697	781	79	10,1 %

In order to process data obtained by using Matlab® software, it was previously set an eliminatory threshold. This corresponds to the value of first quartile of distribution, i.e., to consider an

odorant area as representative it must contain at least 5 odor events. From the totality of 697 odor events, 565 (81%) were distributed within 45 odorant areas that contain at least 5 events per area (figure 4). Consequently, the areas with the number of events lower than the eliminatory threshold have been removed.

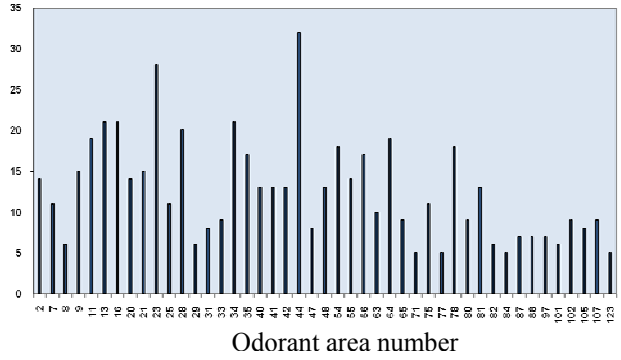

Figure 4. Global aromagram of studied wines.

It can be observed that the odorant areas have well separated peaks (odor events), except the odor events of compounds with a perception threshold inferior to the sensorial capacity of assessors, as well as differences between their ability to recognize a flavor.

The results obtained by GC-O analysis were summarized in table 3.

Table 3. Characteristics of representative odorant areas for studied wines.

Area number*	LRI **	Detection frequency	Odorant area description
2	695	14	Yoghurt, cream, butter
7	766	11	Fruity, solvent
8	770	6	Vinegar, pungent
9	778	15	Fruity, brandy
11	816	19	Fruity, strawberries, pineapple
13	845	21	Cocoa, chocolate, yeasty
16	862	21	Tutti frutti, strawberries, raspberries
20	906	14	Fruity, kiwi, pineapple
21	912	15	Fruit candy, linden, verbena
23	938	28	Peanuts, roasted, banana, pear
25	957	11	Cheese
28	1009	20	Cheese, rancid
29	1014	6	Apple, cheese
31	1027	8	Dried herbs
33	1053	9	Cooked potatoes, gnocchi
34	1060	21	Fruit candy, apple, citrus
35	1074	17	Black currant buds
40	1149	13	Flowers
41	1154	13	Sulfurous, plastic
42	1174	13	Fruity, balsamic
44	1194	32	Lily of the valley, lavender, citrus, marshmallows
47	1235	8	Caramel, chocolate
48	1240	13	Cotton candy, caramel
54	1284	18	Honey, rose, lilac
55	1292	14	Flowers
56	1305	17	Caramel, cotton candy
63	1350	10	Cheese, smoky, dusty
64	1357	19	Spicy, curry, fennel
65	1371	9	Bergamot, citrus
71	1432	5	Licorice
75	1473	11	Floral, herbaceous
77	1489	5	Chemical, pharmaceutical
78	1494	18	Balsamic, clove, curry
80	1508	9	Polyfloral honey
81	1512	13	Prune, floral, smoky
82	1518	6	Clove
84	1529	5	Spicy
87	1545	7	Mineral
88	1550	7	Floral, herbaceous
97	1619	7	Fruity, vegetal
101	1644	6	Sulfurous, fermented
102	1662	9	Vanilla
105	1728	8	Mulled wine, balsamic
107	1748	9	Coconut
123	1909	5	Fruity, berries

** Odorant areas that contain at least 5 events ;*

*** Average LRI in DB-1701 capillary column (30 m x 0.32 mm x 1 μm).*

CONCLUSIONS

Olfactometry analysis (GC-O) allows the selection of odorant compounds using human analyzer, sequentially combining gas chromatography (instrumental analysis) and sensory perception (subjective analysis), thus being a very precious technique for detection of compounds with higher detection threshold than their concentration in wine, and thereby solving some problems in the aroma analysis.

The study presented here has shown that the wines made from white grapes varieties from Republic of Moldova selection (Startovyi, Hibernal and Muscat of Ialoveni) posses a large amount of odorants detectable by olfactometric studies.

The central method of this research was the olfactometry analysis by using the detection frequency method to generate 21 individual aromagrams, which were later summed into a global aromagram for all three wines.

According to mathematical processing of experimental data using Matlab® software, it was established that out of 697 odor events spread in 123 odorant areas, 565 (81%) were distributed within 45 odorant areas that contain at least 5 events per area.

By analyzing the global aromagram, it can be concluded that the odorant areas have well separated peaks (odor events), except the odor events of compounds with a perception threshold inferior to the sensorial capacity of assessors, as well as differences between their ability to recognize a flavor.

In spite of some limitations, The GC-O approach used in the study arises as a valid tool for determining the existence of intense odorants of wine.

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