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Research Article

Chemical Profile Differentiation of Brazilian and Italian Grape Marc Spirits Using Chemometric Tools

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*This work is dedicated to the memory of Professor Douglas W. Franco (in memoriam)

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Keywords
- Grape marc spirits; Chemical profile; Traceability; Chemometrics; Geographical origin

Abstract

Twenty-one samples of grape marc spirits, fifteen from Italy (Grappa) and six from Brazil (Graspa) were analyzed to verify the content of 28 chemical compounds by GC-MS and GC-FID in order to evaluate their differences. The analytical data obtained were subjected to Analysis of Variance (ANOVA), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). ANOVA results showed that diethyl succinate, methanol, propanol and isoamyl alcohol presented different significance at 95%. The PCA and HCA treatment led to a discrimination of the two groups of grape marc spirits based upon the chemical differences found between their distillates. Although both distillates were obtained from the same raw material, the chemical description of each distillate allowed the traceability of their geographic identity

PRACTICAL APPLICATION

Chromatography analysis followed by Chemometric tools were employed to establish the geographical origin of 21 grape marc spirits being 15 Grappa from Italy and the others 6 produced in Brazil. Hierarchical cluster analysis and principal component analysis were performed highlighting the chemical markers of each distillate that allowed the traceability of the grape marc spirits.

INTRODUCTION

Grape pomace distillates are beverage spirits produced from *"vinaccia"* (skins, seeds, stalks, stems and stalks from grapes) being found in most European countries where there is traditional wine production. The European Union established the regulation concerning the definition, denomination, and production of these alcoholic beverages establishing that in Spain, for instance, the denomination *Orujo* as geographic indication for their distillates should be employed. In France the grape pomace are named *Marcs*, in Greece *Tsipouros*, in Portugal *Bagaceiras*, in Yugoslavia *Kommovica*, in Turkey *Raki* and in Italy are known as *Grappas* [1-4]. Geographical Indication (IG) isusually recognized as a qualification strategy since it includes traditions, customs, knowledge, practices and other factors associated with a territorial identity and its geographical origin.

Grappa is an alcoholic distillate of commercial, cultural and historical importance, uniquely produced in Italy. The Italian Legislation defines *"vinaccia"* as the complex containing the solid parts of the grape, like peelings and grape seed, in the presence or not of the stem; but it is only the peeling with must incorporated in it that provide almost all compounds which, by distillation, characterize the distillate. The process of production of Grappa starts with the harvesting and grape crushing. The most is then separated from the grape pomace mainly composed by grape skins and seeds, with or without rasp. The pomace is put in cooper stills (alembics) that are warmed in different ways, starting the distillation process. The distilled can be submitted to an aging process using wooden containers, which contribute with different flavors enrichment. In average, 100kg of grape pomace yields from 4 - 8 liters of pure grappa at 70% (v/v), which is normally further diluted to 45% (v/v) [1-4].

Brazil produces a similar alcoholic distillate, also from grapes, employing a production system similar to the Italian one, which is known as graspa. According to the Brazilian legislation, graspa has an alcoholic content ranging from 35% - 54% v/v, at 20ºC, being obtained from simple alcoholic distillates of grape marc, with or without wine lees, and can be partially or selectively rectified. It is allowed to cut with potable ethyl alcohol from the same origin to regulate the congener's contents [5].

The chemical composition of spirits like grappa, cachaça, cognac, whiskies, as well as several others, is influenced by several factors as for instance the varietal origin of the raw material, its storage conditions, the fermentative step, the distillation technology, the aging time, and the different wood casks used in the aging process. Consequently the chemical profile of the distillates is responsible by its characteristic bouquet [6-12]. In spite of a rigorous quality control about food and beverages

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production by the international community, the concentration of compounds that might present carcinogenic properties, including pesticide residues and carbamates, as example, must be constantly evaluated [13-17].

For years the USA market was invaded by products generically named grappa, frequently presenting very low quality that ruined grappa's image and creating a strong rejection to this beverage. Just from '80s and '90s that grappa began recuperating its reputation, which happened in sync with the boom of Italian wines in the USA culture, which demanded a product with high quality.

In order to avoid any misunderstandings regarding to provenance of its products, the chemical traceability has allowed the pattern recognition of every step of the production of foods, beverages and other products, ensuring the consumer protection, its geographical traceability and, consequently its quality [18-20]. The aiming of this manuscript is to describe the chemical profile of 28 target compounds present in 21 samples of Grappa (Italy) and Graspa (Brazil) in order to establish differences on the chemical composition between these types of distillates. In addition, this work includes the development of statistical tools able to identify theirs geographical origin based on multivariate analysis.

MATERIALS AND METHODS

Samples

All samples of grape marcs were collected from the producer at the moment of the distillation and stored under refrigeration (6-8°C), hence eliminating variables such as aging time, addition of water, or storage effects. The samples were stored in glass bottles, protected from light and kept at 4°C. All analyses were performed in duplicate.

Reagents

The reagents ethyl acetate, butyl acetate, isopentyl acetate, ethyl valerate, ethyl caproate, ethyl lactate, ethyl caprylate, ethyl 3-hydroxybutyrate, ethyl caprate, ethyl 2-furoate, diethyl succinate, isoamyllaurate, methanol, 2-butanol, propanol, isobutanol, isoamyl alcohol, acetic acid, linalol, α-terpineol, β-citronellol, geraniol, α-ionone, ɣ-octalactone, eugenol, farnesol, ethyl carbamate, all of standard analytical grade, were obtained from Fluka, Sigma–Aldrich (St. Louis, Mo., U.S.A.).

Analytical methods

Higher alcohols and acetic acid analysis: Methanol, propanol, isobutyl alcohol, 1-butanol, 2-butanol, isoamyl alcohol, hexanol, and acetic acid were determined according to [21], through direct injection of 1.0μL aliquots of the sample spiked with 4-methyl-1-propanol (internal standard-126 mg/L) into a gas chromatograph system (Hewlett-Packard, HP 5890-A GC) using a flame ionization detector (FID) and a HP-FFAP column (cross-linked polyethylene glycol esterifies, 50 m x 0.20 mm x 0.33 μm film thickness). The analyses were performed at a 1:50 split ratio, using hydrogen as carrier gas (flow rate of 1.2 mL/min). The temperatures of both injector and detector (FID) were set at 250°C. The oven temperature program started at 40°C for 2 min, followed by an increase to 150°C at 10°C/min, an isothermal period of 4 min, an increase to 200°C at 5°C/min, and a maintenance period of 15min.

Ethyl carbamates analysis: Determination of the ethyl carbamate concentration was performed as previously described by [22], through direct sample injection without previous treatment into a gas chromatograph model GC17A (Shimadzu, Tokyo, Japan) hyphened to a mass-selective detector model QP 5050A (Shimadzu, Tokyo, Japan) using electron impact (70 eV) as the ionization source. The mass spectrometer detector operated in the SIM mode (m/z 62) and propyl carbamate was used as an internal standard (150μg L^{-1}**)**. The inlet and detector interface temperatures were 250°C and 230°C, respectively. The oven temperature was programmed to 90°C (2 min); 10 °C/min to 150°C (0 min); 40 °C/min to 230°C (10 min). The injected volume was 1.0 μL in the splitless mode. The ethyl carbamate quantification was carried out through authentic standard addition.

Esters, terpene, lactone and ionones analysis: Determination of ethyl acetate, butyl acetate, isopentyl acetate, ethyl valerate, ethyl caproate, ethyl lactate, ethyl caprylate, ethyl 3-hydroxybutyrate, ethyl caprate, ethyl 2-furoate, diethyl succinate isoamyl laurate, linalool, α-terpineol, β-citronellol, geraniol, α-ionone, y-octalactone, eugenol and farnesol, were carried out in a gas chromatograph model GC20I0 (Shimadzu, Tokyo, Japan), hyphenated to a mass selective detector model QP 20I0 PLUS (Shimadzu, Tokyo, Japan) using electron impact (70 eV) as the ionization source. O-cymene was used as an internal standard. The target analytes were separated through a capillary column coated with an esterifies polyethyleneglycol phase (HP-FFAP; 50,0m x 0,20mm x 0,33um film). The oven temperature was programmed to 60°C (2 minutes); 10°C/min to 210°C. The inlet and detector interface temperatures were 220°C and 230°C, respectively. The injected volume was 1.0 μL in the splitless mode.

Statistical and multivariate analyses: Analysis of variance (ANOVA) with significance level of 95% (α = 0.05) was preliminarily used for the identification of the statistically significant differences among the secondary compound mean concentration values in the alembic fractions. The ANOVA results were checked using Tukey's test.

Principal Component Analysis (PCA) was used in the exploratory analysis to project the data set in a smaller number of variables aiming to simplify the representation of the information. This overview may reveal groups of observations, trends, and outliers and uncover the relationships between observations and variables [23,24].

For Hierarchical Cluster Analysis (HCA), an agglomerative hierarchical method is used to join the clusters, indicating the level of similarity between them. In this procedure, Ward's linkage method was used to determine the distance between clusters and the Euclidian distance for their amalgamation [23].

The data matrix for the chemometric treatment was structured using all data sets (Table 1). The matrix rows represent the chemical compounds concentrations while the columns correspond to the number of grape marcs samples. Samples that presented concentrations < LOD (lower than the

Table 1: Analytical results obtained for standard deviation (SD), P-values (α = 0,05), mean, maximum and minimumvalues of concentration for chemical composition (mg L^{-1}) and alcohol contents (%v/v) in grape marcs from Italy (Grappa) and Brazil (Graspa).

	Grappa							**Graspa**			
	Mean	**Average**	**Maximum**	**Minimum**	**SD**	**Mean**	**Average**	**Maximum**	**Minimun**	**SD**	**p-value**
Ethyl acetate	1.48	1.84	5.39	0.52	1.26	2.81	2.99	6.13	0.09	2.09	0.133
Butyl acetate	0.03	0.03	0.03	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Isopentyl acetate	0.44	0.39	0.85	0.04	0.26	0.18	0.19	0.34	0.05	0.10	0.084
Ethyl valerate	0.05	0.04	0.06	0.01	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ethyl caproate	0.08	0.12	0.31	<LOD	0.11	0.03	0.04	0.11	0.01	0.04	0.104
Ethyl lactate	0.23	0.33	1.14	0.01	0.37	0.29	0.30	0.68	0.02	0.25	0.963
Ethyl caprylate	0.73	0.90	2.63	0.01	0.73	0.37	0.35	0.45	0.15	0.11	0.088
Ethyl 3-hydroxybutyrate	0.10	0.13	0.30	<LOD	0.13	0.04	0.07	0.17	0.02	0.07	0.769
Ethyl caprate	1.29	1.98	7.46	0.05	2.04	0.66	0.62	0.82	0.25	0.21	0.124
Ethyl 2-furoate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diethyl succinate	0.13	0.24	0.67	0.01	0.23	1.35	1.41	3.38	0.04	1.29	0.002
Isoamyllaurate	0.05	0.05	0.08	0.04	0.01	0.04	0.04	0.05	0.04	0.00	0.096
Methanol	1459	1418	2432	256	678	752	771	1263	404	323	0.039
2-butanol	85.2	154	508	54.1	151	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propanol	183	188	321	69.7	65.1	130	129	154	97	21.6	0.046
Iso-butanol	205	229	434	69.2	87.7	292	294	358	246	42.2	0.102
Isoamyl alcohol	568	693	1657	163	417	1322	1239	1607	622	334	0.01
Acetic acid	250	331	1176	31.1	344	144	152	263	43.4	75.3	0.612
Linalol	0.30	0.87	6.60	0.02	1.71	0.13	0.13	0.19	0.07	0.04	0.338
α-Terpineol	0.47	0.87	4.12	<LOD	1.21	1.10	1.10	1.48	0.61	0.29	0.655
β-Citronellol	0.30	0.61	2.19	0.02	0.66	0.71	0.74	1.07	0.53	0.19	0.662
Geraniol	0.20	0.24	0.57	<LOD	0.17	0.11	0.10	0.14	0.00	0.05	0.148
α-Ionone	0.006	0.004	0.01	<LOD	0.01	0.01	0.01	0.01	0.01	0.00	0.631
γ-Octalactone	0.003	0.002	0.008	0.001	0.003	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eugenol	0.05	0.07	0.38	0.04	0.09	0.05	0.05	0.06	0.05	<LOD	0.621
Farnesol	0.07	0.29	2.56	0.01	0.68	0.51	0.50	0.57	0.38	0.07	0.42
Ethyl carbammate	61.7	61.7	80.0	43.3	25.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Alcohol Content (v/v %)	38.0	37.0	40.9	27.3	3.35	37.0	38.1	48.3	32.0	5.48	0.576

limit of detection) in the data set matrix were set to zero (0.00). The pre-processing of the data set in the X-matrix was auto scaled. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed using the Minitab® 17.1.0 (State College, PA - USA).

RESULTS AND DISCUSSIONS

The analytical and statistical obtained data (28 organic compounds and p-values) for 21grape marc samples are presented in Table 2. According to ANOVA, due to the high standard deviation values among the evaluated chemical compounds, just diethyl succinate (0.002 mg L^{-1}), methanol (0.039 mg L^{-1}), propanol (0.046 mg L^{-1}) and isoamyl alcohol (0.010 mg L^{-1}) presented different significance at 95% (p-values) between the grape marcs from Italy and Brazil. Tukey's multiple comparison method was used to corroborate with ANOVA test results.

The high standard deviation values observed cannot be attributed to the experimental analytical procedure. These results suggest that the production process is not uniform by itself since there are many independent variables whose strict control is very difficult to assure, as already verified by us [9].

The ethanol concentration determined was, as expected for all alcoholic beverages, the most abundant volatile compound in both grappa (37% v/v) and graspa (38% v/v) samples (Table 2).

Higher alcohols and most esters are produced during the alcohol fermentation step and the level of these compounds can be managed according to the grape variety, fermentation and distillation conditions. These volatile compounds can be positively associated with the sensory quality of the spirits when not present at high concentrations [1-3,25-30]. Methanol is naturally found in several distilled spirits such as grape marc and the origin of this compound can be associated to the enzymatic degradation of pectin and with the employed process [9,31,32]. It is toxic to humans causing liver injury, neurological intoxication,

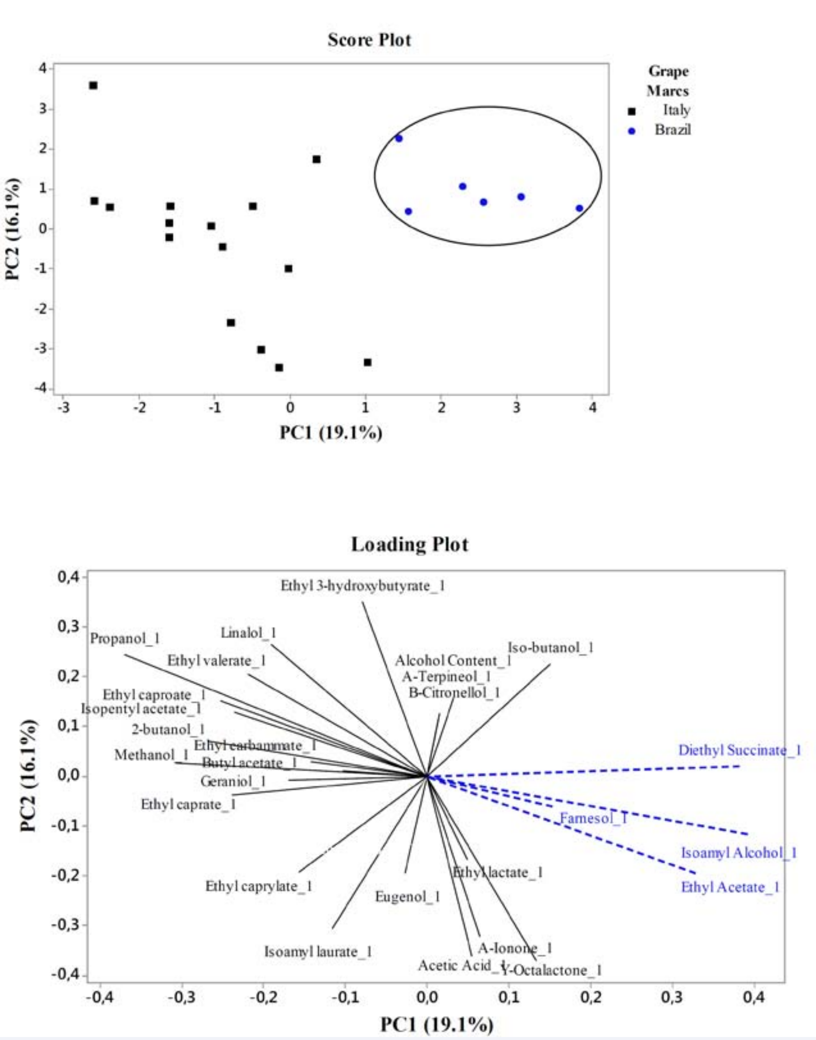

Figure 1 PCA applied in the chemical data of grape marcs from Italy (■) and Brazil (●). Score plot (up) and Loading plot (down).

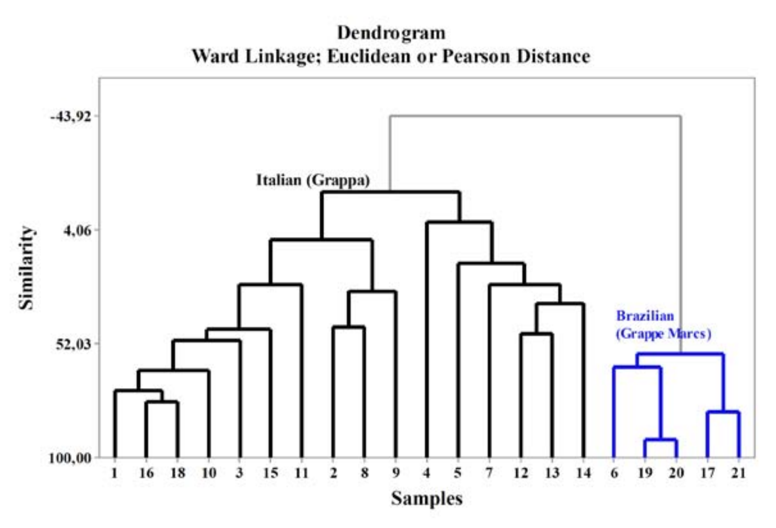

Figure 2 Dendrogram from HCA applied to the chemical data obtained from of grape marcs originated from Italy (grappa) and from Brazil (grappe or graspa).

and convulsive state, depending on the amount ingested. Because of this, the maximum concentration of methanol in these beverages is fixed by many government agencies around the world (ECC 1576/89, INMETRO). Methanol was much more abundant in grappa (1418 mg L^{-1}) than in grasp as (771 mg L^{-1}) while isoamyl alcohol presented higher concentration in the graspas (1239 mg L^{-1}) (Table 2). However, there were no significant differences in mean concentration of both compounds. Although high concentrations of methanol were found in both distillates, no samples presented concentration above to maximum legally permitted values. The others higher alcohols evaluated in this study were 1-propanol, 2-butanol and isobutanol. Among these, only the 2-butanol was not detected in graspa samples (Table 1).

The high concentrations of acetic acid can be associated to potential bacterial contamination and presents sour taste and pungent smell. The grappa samples (331 mg L^{-1}) exhibited acetic acid concentration about 100% higher than the graspa ones (152 mg L^{-1}).

Among the esters here evaluated, the concentrations of ethyl acetate and ethyl lactate were as abundant in graspa as in grappa. The others, butyl acetate, isopentyl acetate, ethyl valerate, ethyl caproate, ethyl caprylate, ethyl 3-hydroxybutyrate, ethyl caprate, ethyl 2-furoate, diethyl succinate and isoamyllaurate presented higher mean concentrations in the grappa samples (Table 2).

Terpenes are found in essential oils of flowers, fruits and are common constituents of flavorings and fragrances. The presence of terpenes in the distillated is usually associated to the fermentation process and their concentration has been used to attest the sensorial quality of wines, beers and distilled beverages [33-36]. In this report, among the terpenes the concentration of α-terpineol, farnesol, β-citronellol, geraniol, were found to be higher in the graspa samples. The eugenol and linalool concentrations were more abundant in grappa than in graspa samples.

Ionones and lactones present high potency and varied

Table 2: Chemical composition (mg L^{-1}) and alcohol content (%v/v) of grape marcs from Italy and Brazil.

	Italy (Grappa)															Brazil (Graspa)					
Chemical Compounds	**IG1**	**IG2**	**IG3**	**IG4**	**IG5**	**IG6**	**IG7**	**IG8**	**IG9**	**IG10**	**IG11**	**IG12**	**IG13**	**IG14**	**IG15**	**BG1**	**BG2**	**BG3**	**BG4**	**BG5**	**BG6**
Ethyl Acetate	0.9	1.78	1.93	0.64	1.87	5.39	1.48	0.97	2.13	1.46	1.33	3.64	1.13	2.44	0.52	1.74	6.13	0.09	2.65	2.96	4.39
Butyl Acetate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.03	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Isopentyl Acetate	0.44	0.85	0.55	0.82	0.46	0.46	0.22	0.26	0.67	0.07	0.45	0.27	0.17	0.12	0.04	0.13	0.34	0.05	0.17	0.19	0.26
Ethyl Valerate	<LOD	0.01	<LOD	0.06	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ethyl Caproate	0.03	0.09	0.31	0.31	0.23	<LOD	0.08	0.04	0.03	0.08	0.26	0.02	0.04	0.1	<LOD	0.11	<LOD	<LOD	0.04	0.01	0.02
Ethyl Lactate	0.02	0.25	<LOD	0.3	0.01	1.14	0.2	0.93	0.08	0.03	0.01	0.12	0.55	0.7	0.27	0.06	0.68	0.02	0.25	0.32	0.47
Ethyl Caprylate	0.29	0.73	1.08	0.69	2.63	0.14	0.49	1.02	0.37	0.37	0.93	2.14	1.17	1.35	0.01	0.45	0.44	0.15	0.35	0.31	0.4
Ethyl 3-Hydroxybutyrate	0.1	<LOD	<LOD	0.3	<LOD	<LOD	<LOD	0	<LOD	<LOD	<LOD	<LOD	0.1	<LOD	<LOD	0.17	<LOD	<LOD	0.06	0.02	0.03
Ethyl Caprate	0.62	1.66	1.29	2.74	4.18	0.11	0.28	7.46	0.96	0.47	0.39	3.16	2.82	3.55	0.05	0.76	0.82	0.25	0.61	0.56	0.72
Ethyl 2-furoate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diethyl Succinate	0.03	0.13	0.01	0.04	0.26	0.47	0.37	0.54	0.06	0.08	0.04	0.38	0.67	0.49	0.05	0.04	3.38	0.08	1.16	1.54	2.27
IsoamylLaurate	0.05	0.04	0.05	0.06	0.05	0.04	0.07	0.04	0.04	0.04	0.05	0.08	0.07	0.05	0.05	0.04	0.05	0.04	0.04	0.04	0.05
Methanol	696	2088	1459	696	1040	256	1325	2388	1877	1572	2432	821	1577	869	2167	465	1263	404	711	793	987
2-butanol	<LOD	508	<LOD	81	<LOD	85	<LOD	185	86	172	<LOD	<LOD	62	<LOD	54	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propanol	220	253	139	277	141	145	70	321	183	191	225	117	178	207	152	154	97	150	133	127	115
Isobutanol	252	200	205	362	434	69	185	228	148	181	295	273	220	201	177	246	358	252	285	299	322
Isoamyl Alcohol	988	352	351	475	1657	890	914	525	163	221	758	1260	568	927	344	622	1607	1288	1172	1356	1390
Acetic Acid	<LOD	<LOD	<LOD	<LOD	<LOD	245	1176	31	44	367	51	580	179	381	256	113	263	43	140	149	202
Linalol	1.28	0.28	0.09	6.6	0.9	<LOD	0.02	0.55	0.07	0.06	0.16	0.37	0.33	0.14	1.29	0.19	0.07	0.16	0.14	0.13	0.11
α-Terpineol	0.22	0.36	0.05	3.3	0.66	0.34	1.22	0.53	0.05	0.12	0.47	0.81	0	0.84	4.12	1.12	1.48	0.61	1.07	1.06	1.28
β-Citronellol	0.88	0.27	0.2	2.19	1.37	0.03	0.02	0.53	0.13	0.2	0.36	1.75	0.25	0.73	0.3	0.53	0.61	1.07	0.74	0.81	0.67
Geraniol	0.18	0.13	<LOD	0.33	0.57	<LOD	<LOD	0.37	0.2	0.03	0.1	0.28	0.18	0.25	0.54	0	0.14	0.12	0.09	0.12	0.11
α-Ionone	<LOD	<LOD	<LOD	0.001	0.005	0.014	<LOD	0.001	<LOD	<LOD	<LOD	0.011	0.002	0.003	0.011	<LOD	<LOD	0.01	<LOD	<LOD	<LOD
ɣ-Octalactone	<LOD	<LOD	<LOD	<LOD	0.002	0.008	0.001	<LOD	<LOD	<LOD	0.001	0.003	0.001	0.004	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Eugenol	0.043	0.045	0.044	0.044	0.064	<LOD	0.381	0.048	0.044	0.048	0.049	0.057	0.058	0.06	0.047	0.06	0.05	0.05	0.05	0.05	0.05
Farnesol	0.03	0.09	0.07	0.02	2.56	0.01	0.01	0.12	0.13	0.07	0.04	0.71	0.02	0.18	<LOD	0.57	0.54	0.38	0.5	0.47	0.52
Ethyl Carbamate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.08	<LOD	0.043	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Alcohol Content	38.8	35.7	39.1	36.4	40.1	38.5	27.3	40.9	36.8	36.9	35.8	38.9	39.4	38	33.2	48.3	36.4	32	38.9	35.7	37.6

sensory properties being therefore important flavor compounds in many food and beverages. The α-ionona presents violet-like, fruity, raspberry-like and flowery as odorant characteristics. The organoleptic proprieties of γ-octalactone are associated with coconut; creamy; peach; sweet. The concentrations of α-ionona (6.0 μg L^{-1}) and γ-octalactone (3.0μg L^{-1}) were quantified only in grappa samples while for all graspa samples, when present, the verified concentrations were well below the limit of detection of the employed method.

Ethyl carbamate (EC), known also as urethane, is generally found in fermented foods (bread, yogurt, wine and beer) and in distilled spirits like whisky, cachaças, and rum. It is mainly formed by a spontaneous chemical reaction of ethanol with urea. Studies correlated its presence to carcinogenic effects, being its presence in foods and beverages being monitored in many countries. Just grappa samples presented detectable ethyl carbamates concentrations (61.7 μg^{-1}) [14].

PCA and HCA were performed aiming determining the clustering using the correlation between the chemical profile and the grape marc samples. In Figure 1 it can be observed the clustering of these samples (Scores plot) and the chemical descriptors responsible for it (Loading plot). The first three PCs (PC1, PC2, and PC3) accounted for 19.1%, 16.1%, and 10.7% of the total variance, respectively. However, the total variance observed in the PCA for the first nine principal components (PCs) with eigenvalues greater than 1 was 88.4% [37]. According to the loading plot shown in Figure 1, most grape marc samples from Italy presented higher concentrations of propanol, linalool, ethyl valerate, ethyl caproate, isopentyl acetate, 2-butanol, methanol, geraniol, ethyl caprate, , ethyl lactate, isoamyllaurate, while most of grape marc samples from Brazil presented higher concentrations of farnesol, diethyl succinate, isoamyl alcohol and ethyl acetate (Figure 1).

The generated dendrogram (Figure 2) displays the groups formed by clustering of grape marc samples and their similarity levels. Two clusters can be observed when the Ward's distance algorithm is used to the linkage method (since the data set has high standard deviation values) and Euclidian distance or Pearson Correlation in the amalgamation step. The results to HCA correctly fitted 85.7% of the grape marc samples (15 Italian grappa, and 4 Brazilian grape marcs) when diethyl succinate, isoamyl alcohol, farnesol, ethyl acetate, linalool, ethyl valerate, propanol, ethyl caproate, isopentyl acetate, 2-butanol, ethyl carbammate, methanol, butyl acetate, geraniol, ethyl caprate, ethyl caprylate, ethyl 2-furoate, isoamyllaurate and eugenol were used as chemical descriptors. The Brazilian grapes marcs cluster presented the highest similarity level.

CONCLUSION

The results obtained in this investigation indicate that is possible, based on the chemical profile of grape marcs, identify the geographic origins of grappa produced in Italy and Brazil. Although both distillates are obtained from grapes, the differences observed among the chemical grape marc samples can be associated to the edaphoclimatic factors differences (e.g., soil composition, temperature, water), beside the differences during the production steps. The concept evaluated in this study can be extended to include grape marc samples produced in other countries in order to identify and characterize each sample according to their geography origin.

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