Analytical Characterization of Madeira Wine

J. M. F. Nogueira*,† and A. M. D. Nascimento‡

Departamento de Química e Bioquímica, CiTecMat, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal, and Laboratório Agrícola da Madeira, Estrada Eng. Abel Vieira, 9135 Camacha-Madeira, Portugal

For a correct characterization of Madeira wine commercially available in the market, 52 samples having different types and ages, representative of the delimited region of Madeira (liquor wine of quality produced in delimited region), were analyzed in relation to physicochemical and sensorial parameters. Standard methodology for spirits and alcoholic beverages as well as a council of tasters were adopted respectively to quantify such parameters, according to European Union regulations. The main physicochemical parameters analyzed demonstrated that Madeira wine represent a high quality beverage without toxicological risks, as all constituents have in general contents clearly below the maximum concentration admissible by the national and/or international rules. A reasonable differentiation of properties could be achieved between samples having different types and ages, when principal component, discriminant and cluster analyses were applied to the analytical data, especially for physicochemical parameters.

Keywords: *Madeira wine; physicochemical analysis; sensorial analysis; quality control; differentiation; multivariate analysis; principal component analysis; discriminant analysis; cluster analysis*

INTRODUCTION

The temperate to subtropical Island of Madeira, with a surface area of 741 km^2, is set far out in the Atlantic ocean, some 600 km due west of the Moroccan coast and 978 km to the southwest of Lisbon.

Since the 17th century, this Portuguese island produced some of the most famous wines, commercially known all over the world as Madeira wines. At that time, Madeira became known as the "island of wine".

Madeira Island is by soil nature volcanic, the orography is accentuated and vegetation abundant due to the humidity and mildness of the climate. It is mainly on the sunny hillsides of the south side of Madeira island in specific areas, especially in terrace steps named "poios", which are extended on the slopes from high up down to the sea's edge, that the main traditional varieties of *Vitis vinifera* grapes, Sercial, Verdelho, Boal, Malvasia, Terrantez, and Bastardo, are cultivated from which Madeira wine is made (Vieira, 1991), Tinta Negra Mole being the recommended variety most frequently used at present, due to the grape diseases that appeared in the past.

Initially Madeira was not a fortified wine, but gradually the addition of natural grape spirit, containing 95% (v/v) ethyl alcohol (EU No. 3111, 1993), became a common practice in order to stabilize the wines during the long voyage to distant markets.

Madeira, a excellent aperitif and dessert wine, whose alcoholic content lies between 17 and 22, is commercially available in different types specially dry, medium dry, medium sweet (medium rich), and sweet (rich) in relation to the sugar content, according with the period of must fermentation which is stopped by the addition of natural grape spirit. The four basic types of Madeira are each named after the main grape variety from which they are made. Malvasia, fortified early in order to retain the richness, which is its hallmark, is a rich dark colored and robust wine, distinctly sweet and mellow. Boal, fortified after approximately half the sugars have been converted to alcohol, is a full bodied and fruited wine with a well-rounded flavor and attractive smoky complexity. Verdelho ferments still further and is a tangy fine textured wine, elegant and dry. Sercial, the driest Madeira, light in color and scented, is allowed to ferment until completely dry.

Madeira wine has a long life, having in the consideration of aging several categories, as 3 (*Finest*), 5 (*Reserve*), 10 (*Old Reserve*), 15 (*Extra Reserve*), and more than 20 years old (*Vintage)*, made only with the very finest wines from a exceptionally good year and exclusively from one of the traditional grapes varieties (Read, 1995). These wines have to remain in cask for a minimum of 20 years after which they spend a further 2 years in a bottle. The remarkable longevity of Madeira is best exemplified by the *Vintage*, which can remain in excellent condition for 150 years and longer still in some cases.

The physicochemical and organoleptic or sensorial characteristics of such generous wines depends on several factors concerning the specific area of production, climate, volcanic nature of the soil, and grape varieties as well as the production techniques according to the winery practice. Since the 18th century, the fermentation has taken place in a cubical concrete or stainless steel tank or, for small producers, in wooden casks with temperature control. Fermentation is arrested by the addition of spirit when the appropriate amount of natural grape sugars has been fermented out. Following fermentation, for aging, Madeira wines are stored in casks and vats in a special lodge ("estufas") which are gradually heated between 45 and 55 °C for

† Universidade de Lisboa (fax 351 1 7500088; e-mail nogueira@fc.ul.pt).

‡ Laboratório Agricola da Madeira.

10.1021/jf9804490 CCC: $18.00
Published on Web 01/29/1999

at least 3 months; such a procedure is generally called the baking conditions. After this period, the temperature of the wine is allowed to fall and begin the normal maturation in oak casks or the aging process occurs, by sun influence ("Canteiro" wine), in an oak cask for a minimum of 2 years (Lopes, 1994).

The quality control of the main enological parameters of such commercially available wines, according to European Union (EU) regulation (EU No. 822, 1987), is almost inexistent in the literature. Indeed, it is very important to quantify the main constituents, which some of them when higher than the maximum concentration admissible (MCA) by the national and/or international rules could represent a toxicological danger to public health. On the other hand, the physicochemical and sensorial parameters must also be definitely controlled as a strategy to confirm the authenticity and in order to prevent or detect possible adulterations, due the current high exportation around 32 000 hL/year, as well as the high prices achieved by these quality wines.

The aim of the present work was to characterize for the first time Madeira wine commercially available in the market, representative of the delimited region of Madeira (*vlqprd*) (EU No. 3111, 1993), according with different types and ages. To improve the quality control of such wines, the evaluation of the main physicochemical and sensorial parameters were established with accurate criteria of differentiation, using for such intent multivariate techniques of data analysis (Hair et al., 1995; Livingstone, 1995; Manly, 1997).

EXPERIMENTAL PROCEDURES

Materials and Reagents. All reagents used were commercially high grade with more than 97% purity or according with the purity established in the standard methodology adopted for physicochemical analysis.

Fifty-two samples of four different Madeira wine types (dry, medium dry, medium sweet, and sweet) from six growers and with several ages of each (five with 3 years old (*Finest*), four with 5 years old (*Reserve*), and four with 10 years old (*Old Reserve*)) were obtained from the Madeira Wine Institute. To some of them aging conditions and chemical corrections were implemented during the wine growing, according to EU regulations (EU No. 4252, 1988).

Methodology and Instrumentation. *Physicochemical Analysis.* The methodology adopted to analyze the physicochemical parameters of Madeira wine samples was in agreement with EU regulation for quality wines produced in delimited regions (*vlqprd*) (EU No. 823, 1987) and according with the "Portuguese Official Standards for Spirits and Alcoholic Beverages" (NP 2139, 1987; NP 2140, 1987; NP 2141, 1987; NP 2142, 1986; NP 2143, 1987; NP 2220, 1987; NP 2221, 1987; NP 2222, 1987; NP 2226, 1987; NP 2227, 1987; NP 2228, 1988; NP 2279, 1988; NP 3263, 1990; NP 3381, 1990) and other international organizations of standardization (Ribéreau, 1982; Garcia, 1988). Due to absence of official regulation, the standard methodology from "Office International de la Vigne et du Vin" (OIV, 1990) was adopted.

For residue determination, a multiresidue method with several high-grade standard pesticides was adopted, using capillary gas chromatography (CGC) amenable to electronic capture (ECD) and mass spectrometry (MSD) detectors (Guide FAO7OMS, 1985; Garcia, 1988; Cabais, 1991).

Table 1 present the standard methodology and the main instrumentation used, as well as the physicochemical parameters analyzed. All analysis was done in triplicate.

Sensorial Analysis. A council of six tasters with extensive experience made the sensorial analysis according to the parameters advised by EU regulation (EU No. 823, 1987; Garcia, 1988; Martins, 1998), during six sessions before lunch at the Madeira Wine Institute. The parameters analyzed were *sight* (depth of color and limpidity), *smell* (intensity, quality, and strange aromas), *taste* (sweetness, acidity, bitter, quality, body, finish, and strange tastes), and *global appreciation* (tipicity). The 52 samples were tasted at room temperature, according to an increasing order of sweetness and aging. To avoid influencing the council tasters, a random number was attributed to each sample and a centesimal scale was adopted for the wine classification, which ranged between poor and outstanding.

Multivariate Analysis. For principal component (PCA), discriminant, and cluster analysis, the data from physicochemical and sensorial parameters were standardized and used as variables for object description. The objects were the 52 Madeira wine samples having different types, as dry (D), medium dry (MD), medium sweet (MS), and sweet (S), with three categories of aging, as 3, 5, and 10 years old.

The data matrix was used for computerized multivariate analysis of data, as PCA, discriminant, and cluster analysis, by the software package STATISTICA for Windows from StatSoft, Inc. (Tulsa, OK).

RESULTS AND DISCUSSION

Physicochemical Characterization. The physicochemical parameters analyzed, taking in consideration the MCA in agreement with EU regulation for commercialization (EU No. 4252, 1988), were subdivided as *acidic*, *alcoholic and phenolic*, *glucidic and extract*, *mineral and sulfur dioxide*, and *volatile* composition, to achieve an easy criteria of systematization and to better compare the results obtained. Table 2 shows the resume of the average data (mean $\pm$ SD) from the physicochemical analysis, which could characterize Madeira wine samples studied, according to type and aging (Nogueira, 1997).

The *acidic* composition showed an average pH values almost invariant for all samples studied, which lies between 3.26 and 3.42 (20 °C). The average content of total and fix acidity seems to increase with aging for all types of Madeira wine, especially for samples 10 years old. Volatile acidity, which reflects the acetic acid content from the fermentation process, also presented a similar behavior, where the average content increased naturally with the age for all types but below the MCA established, 1.2 g/L for samples up to 10 years old (Jornal Oficial da Madeira, 1994). The main acid from grape, tartaric acid, presents an average content very similar for all types and ages, showing a higher level especially for medium dry and medium sweet samples, but all data present values below the MCA established, which according to several authors is 4 g/L (Garcia, 1988).

The *alcoholic and phenolic* composition, taking into consideration the acquired volumetric alcoholic degree, observed by aerometry (20 °C), shows for all types average values up to 18% for younger samples, but a small increment above 19% could be observed for Madeira wines 10 years old. Such observation is in agreement with EU regulation (EU No. 4252, 1988), which established values among 15% and 22% for liquor wines. The average of total polyphenols measured, using the Folin−Ciocalteu colorimetric index (IFC) adopted by OIV, showed values which increase slightly with the sugar content.

The *glucidic and extract* composition, as was expected, showed an average content of total sugar which clearly increased with the sweetness degree, which lies between 47.98 and 122.50 g/L, but a very small decrease is in

Table 1. Standard Methodology and the Main Instrumentation Used for the Determination of the Physicochemical Parameters Analyzed in Madeira Wine Samples

physicochemical parameters	standard methodology	instrumentation
pH (20 °C)	OIV method (potentiometry)	potentiometer Crison 2002
tot. acidity	NP 2139 (acid−base titration)	magnetic stirrer Selecta 379
fix acidity	NP 2141 (diff between tot. and volatile acidity)	-
volatile acidity	NP 2140 (distillation followed by acid−base titration)	alcodest Selecta
alcoholic degree (20 °C)	NP 2143 (distillation followed by aerometry)	thermostatic bath Grant
tot. polyphenols	OIV method (colorimetry)	spectrophotometer Hitachi U 2000
tartaric acid	OIV method (Rebelein method: spectrophotometry)	
5-HMF	NP 3381 (spectrophotometry)	
tot. sugar	Munson and Walker method (gravimetry)	muffle Thermolyne 48000 electronic balance Mettler 35
	automatic segmented flow analysis (photometry)	automatic analyzer Skalar SA 8606−00 auto sampler Skalar 1000 photometer Skalar 6250 water bath Skalar 5501
nonreducing extract	NP 2228 (difference between total sugar and total dry extract)	-
tot. dry extract	NP 2222 (according to density or alcoholic degree)	-
density (20 °C)	NP 2142 (aerometry)	-
Baumé deg (20 °C)	from density conversion	-
ash	NP 2221 (incineration followed by gravimetry)	electronic balance Precisa 40SM 200A muffle Thermolyne 48000
ash alkalinity	NP 2279 (acid−base titration)	thermostatic bath Memmert
chlorides	NP 2226 (potentiometry)	potentiometer Metrohm 691
phosphates	OIV method (colorimetry)	thermostatic bath Memmert muffle Thermolyne 48000 spectrophotometer Hitachi U 2000
sulfates	NP 2227 (gravimetry)	electronic balance Precisa 40SM 200A centrifuge Hettich Universal
SO_2 (free + total)	NP 2220 (Chaine method:iodimetric titration)	thermostatic bath Grant iodomatic Gibertini
methanol ethanal ethyl acetate 2-butanol 1-propanol 2-methyl-1-propanol 2-propene-1-ol 1-butanol 3 methyl-1-butanol + 2-methyl-1-butanol tot. higher alcohols	NP 3263 (capillary gas chromatography)	alcodest Selecta electronic balance Mettler AE 100 chromatograph HP 5890 serie II automatic sampler HP 6890 FID detector capillary column: DB-Wax (J&W scientific) poly(ethylene glycol) (30 m × 0.533 mm i.d. × 1.0 μm film thickness) electronic integrator HP 3396A
residues (pesticides)	multiresidue method (capillary gas chromatography followed by mass spectrometry)	chromatograph HP 5890 serie II ECD detector semicapillary column: HP-1 cross-linked methyl silicone gum (5 m × 0.53 mm i.d. × 2.65 μm film thickness) electronic integrator HP 3396A serie II chromatograph HP 5890 serie II mass detector HP-5971A capillary column: HP-1 cross-linked methyl silicone gum (12 m × 0.2 mm i.d. × 0.33 μm film thickness)

general observed especially for samples 10 years old. The nonreducing extract, taking into consideration all nonvolatile components of the wine in specific physical conditions with the exception of total sugars, showed the same average level both for all ages and types. The total dry extract, density, and Baumé degree (20 °C) observed, the latter generally adopted to classify the type of Madeira wine (Jornal Oficial da Madeira, 1982), present a very small variation for different ages within each type, increasing obviously with the sugar content, as was expected.

The *mineral and sulfur dioxide* composition showed an average content of ash and ash alkalinity very similar to all samples studied. For chlorides, phosphates, and sulfates, the average contents increased a little with the aging, but the same level is observed for each type. Nevertheless, the chlorides and sulfates values are clearly lower than 1000 and 2000 mg/L but some wines showed average phosphate contents a bit higher than 300 mg/L, which are the MCA according to the EU regulation, respectively. Concerning the total and free sulfur dioxide, used in enology as antioxidant and stabilizer as well as antiseptic, the average contents are clearly below the MCA established by EU regulation, 200 mg/L for samples having more than 5 g/L of total sugar content (EU No. 4252, 1988).

The *volatile* composition, which influences very much Madeira wine organoleptic characteristics, indicated that the average content of 5-(hydroxymethyl)furancarbaldehyde (5-HMF), having origin in hexoses, increases clearly both with the sweetness and aging. Methanol from the pectin's hydrolysis, ethanal from the enzymatic decarboxylation of pyruvic acid, and ethyl acetate from the yeast and acetic bacteria metabolism, important constituents of the aromatic profile, were shown by capillary gas chromatography (CGC) to increased with

Table 2. Resume of the Average Data Obtained from Physicochemical Analysis of Madeira Wine Samples, According to the Type and Age

TYPE	Dry			Medium Dry			Medium Sweet			Sweet		
AGE (years) ⇨	3	5	10	3	5	10	3	5	10	3	5	10
COMPOSITION*												
Acidic												
pH (20ºC)	3.31±0.05	3.34±0.04	3.26±0.10	3.35±0.09	3.35±0.08	3.37±0.09	3.35±0.08	3.38±0.08	3.36±0.09	3.41±0.08	3.42±0.08	3.38±0.08
tot. acidity (g/L)	5.72±0.46	5.93±0.50	8.50±1.65	5.82±0.35	6.25±0.52	7.63±0.59	5.80±0.39	6.10±0.36	7.20±1.04	5.34±0.21	5.90±0.40	6.93±0.30
fix acidity (g/L)	5.12±0.44	5.15±0.57	7.25±1.49	5.33±0.45	5.58±0.69	6.68±0.39	5.40±0.60	5.35±0.29	6.00±1.04	4.92±0.23	5.10±0.24	5.85±0.24
volatile acidity (g/L)	0.50±0.07	0.60±0.08	1.00±0.16	0.40±0.14	0.53±0.15	0.95±0.17	0.38±0.11	0.60±0.08	1.00±0.08	0.34±0.11	0.63±0.21	0.88±0.13
tartaric acid (g/L)	1.14±0.21	1.25±0.17	1.50±0.54	1.52±0.22	1.40±0.33	1.48±0.36	1.66±0.30	1.48±0.17	1.70±0.34	1.40±0.25	1.23±0.17	1.40±0.18
Alcholic and Phenolic												
alcoholic degree (% vol.; 20ºC)	18.26±0.55	18.50±0.64	19.33±0.33	18.30±0.57	18.58±0.59	19.20±0.75	18.20±0.69	18.40±0.71	19.03±0.53	18.38±0.63	18.65±0.54	19.38±0.31
tot. polyphenols (IFC)	6.60±1.00	7.15±0.48	7.73±1.64	8.42±1.17	7.90±1.94	8.85±1.18	9.52±1.50	8.75±1.34	9.58±1.13	11.04±2.63	9.48±1.76	8.90±3.99
Glucidic and Extract												
tot. sugar (g/L)	47.98±3.25	48.70±3.07	50.23±9.97	73.98±8.09	71.83±1.68	71.88±0.83	96.10±7.65	94.35±5.46	91.70±5.00	122.50±13.01	120.73±5.73	118.20±6.54
nonreducing extract (g/L)	19.94±1.42	18.65±2.87	24.50±2.11	20.56±2.10	22.35±1.30	23.70±1.61	19.84±1.18	22.38±0.68	24.60±2.19	20.84±4.29	24.63±3.14	28.33±2.60
tot. dry extract (g/L)	67.92±4.30	67.35±5.79	74.73±10.82	94.54±6.44	91.68±5.54	95.58±0.92	115.94±7.32	116.65±5.13	116.28±6.11	143.28±10.70	145.33±3.58	146.48±6.16
density (g/mL; 20ºC)	1.0016±0.0016	1.0013±0.0024	1.0032±0.0040	1.0118±0.0023	1.0114±0.0011	1.0114±0.0009	1.0201±0.0021	1.0202±0.0014	1.0195±0.0023	1.0304±0.0087	1.0334±0.0040	1.0307±0.0024
Baumé degree (20ºC)	0.50±0.21	0.45±0.30	0.78±0.52	2.32±0.30	1.88±0.15	1.90±0.14	3.08±0.28	3.15±0.17	2.98±0.31	4.54±0.50	4.63±0.25	4.53±0.33
Mineral and Sulphur Dioxide												
ash (g/L)	1.97±0.20	2.31±0.30	2.66±0.29	2.13±0.03	2.31±0.30	2.74±0.31	2.11±0.21	2.36±0.16	2.51±0.23	2.03±0.29	2.32±0.38	2.58±0.31
ash alkalinity (g/L)	1.82±0.24	1.95±0.19	2.10±0.18	1.48±0.08	1.58±0.19	1.68±0.15	1.40±0.16	1.63±0.13	1.68±0.28	1.48±0.19	1.63±0.25	1.73±0.21
chlorides (mg/L)	66±12	86±30	126±33	60±8	73±20	113±13	65±10	79±16	98±13	64±15	83±17	103±20
phosphates (mg/L)	306±39	311±58	364±49	295±44	308±18	344±31	307±43	228±20	309±59	286±27	296±13	302±39
sulfates (mg/L)	493±121	611±138	955±158	467±162	505±208	865±145	519±178	614±141	786±127	511±173	610±122	864±167
SO_2 total (mg/L)	25±2	35±7	32±2	38±14	38±8	37±1	40±8	42±9	44±2	39±10	40±5	42±6
SO_2 free (mg/L)	2±0.00	3±0.81	3±0.96	3±0.71	3±0.50	3±0.82	3±2.07	3±0.82	3±1.26	4±2.39	3±1.00	3±1.41
Volatile												
5-HMF (mg/L)	171±131	193±97	275±60	259±140	231±168	366±100	385±175	308±163	577±157	305±197	351±353	525±371
methanol (mg/100mL a.a.)	32±3	39±12	46±3	24±13	26±8	41±10	33±7	40±14	43±2	29±7	36±6	36±4
ethanal (mg/100mL a.a.)	34±5	40±6	63±13	34±6	43±4	61±17	39±9	48±10	65±10	36±5	49±9	61±9
ethyl acetate (mg/100mL a.a.)	56±9	70±3	128±40	41±20	46±15	109±34	44±19	71±16	119±9	42±17	75±24	104±29
2-butanol (mg/100mL a.a.)	0.00	0.28±0.67	1.30±1.41	0.00	0.25±0.58	1.30±1.27	0.00	0.38±0.77	1.55±1.10	0.00	0.65±0.63	0.65±0.75
1-propanol (mg/100mL a.a.)	11.74±3.34	11.60±2.17	14.05±2.39	10.28±3.38	9.03±1.72	11.83±2.63	8.86±3.85	11.98±2.30	13.33±1.88	7.64±3.70	9.85±2.49	10.45±1.83
2-methyl-1-propanol (mg/100mL a.a.)	28.08±2.33	28.03±4.06	34.43±3.16	23.34±4.85	22.68±1.02	30.83±4.37	19.40±7.25	30.48±3.67	29.60±5.73	17.74±7.32	22.40±4.70	25.45±5.33
2-propene-1-ol (mg/100mL a.a.)	0.14±0.31	0.00	0.33±0.65	0.00	0.00	0.55±0.64	0.00	0.00	0.48±0.55	0.00	0.38±0.43	0.30±0.60
1-butanol (mg/100mL a.a.)	0.12±0.27	0.30±0.35	0.48±0.34	0.20±0.27	0.30±0.22	0.45±0.13	0.10±0.22	0.53±0.41	0.93±0.17	0.00	0.13±0.25	0.13±0.25
3-methyl-1-butanol + 2-methyl-1-butanol (mg/100mL a.a.)	83.68±13.85	81.60±10.99	99.80±11.65	65.12±18.30	62.10±10.44	88.68±14.48	52.52±24.25	85.88±14.85	85.73±14.25	48.50±24.86	63.93±14.47	72.23±16.08
tot. higher alcohol's (mg/100mL a.a.)	124±17	122±16	150±15	99±27	94±13	134±23	81±35	129±21	131±20	74±36	97±22	112±26

*: Mean ± Standard Deviation

the aging, especially the last one; but the same concentration is observed within each type. Methanol presents average contents below 150 mg/L, which such limit is in accordance with the OIV recommendation (OIV, 1990). The average content of total higher alcohols presents a general increase with aging, but a decrease within each type is observed, showing values for the individual compounds inside the MCA indicated by several authors (Garcia, 1988), as usually above 50 mg/L for 2-methyl-1-propanol, 3-methyl-1-butanol and 2-methyl-1-butanol (amylics). In addition, 1−50 mg/L is usually found for 2-butanol, 1-propanol, 1-butanol, and 2-propene-1-ol (allylic) (Nogueira, 1996).

The control of pesticide residues, mainly organochlorated, dicarboximides, ftalimides, and piretroides, due application in Madeira agriculture, was checked by CGC and CGC-MS, showing no vestigial traces for all samples studied.

Other important physicochemical parameters, as ethyl carbamate, total of anthocyanins, and metals in particular, were not analyzed as other authors (Ferreira, 1992; Brazão, 1995) reported that no evidence of dangerous concentrations used to be found in Madeira wines commercially available.

Although the physicochemical parameters studied showed important data for the characterization of Madeira wine commercially available, the differentiation according to type and age is quite difficult to establish from the direct observation of Table 2. In recent years, multivariate techniques of data analysis represent a powerful statistical tool to explain wine differentiation, adopted by several authors (Noble, 1980; Freitas, 1988; Vasconcelos, 1989; Vasconcelos, 1990; Rossi, 1994; Garcia, 1996). The physicochemical data were used as variable vectors for multivariate analysis in order to obtain more detailed information on the variables that mainly influence the sample similarities and differences.

In the first approach, PCA was adopted to reduce the number of physicochemical variables, as well as to detect the structure in the relationships between them, which indicates that the first two PCs explain 53% of the variability among all samples studied. The observation of the loading scores in the Table 3 suggests that 14 variables, having coefficients magnitude higher than 0.70, may be enough to adequately describe the samples according to age, as *total acidity*, *fix acidity*, *volatile acidity chlorides*, *ethanal*, *ethyl acetate*, *1-propanol*, *2-methyl-1-propanol*, *3-methyl-1-butanol* + *2-methyl-1-butanol*, and *total higher alcohols*, shown in the PC 1. According to the type, *total sugar*, *total dry extract*, *density*, and °Baumé can adequately describe the samples as shown in the PC 2.

In Figure 1 can be seen the scores plot extracted from the first two PCs derived from a data set of the 14 variables measured on the fifth two samples, from which now explain 66% of the variability contained in both vectors. In fact, the PC 1 axis seems to be responsible for the complete differentiation between dry and sweet samples, and on the other hand, young and old samples are clearly differentiated in the PC 2 axis.

After such considerations, discriminant analysis with emphasis on canonical analysis was employed to determine which physicochemical variables better discriminate between the type and age groups. Figure 2 shows the scatterplot of canonical scores for the first two discriminant functions (root 1 and root 2), which explains 95.5% of the variability, where can be seen a

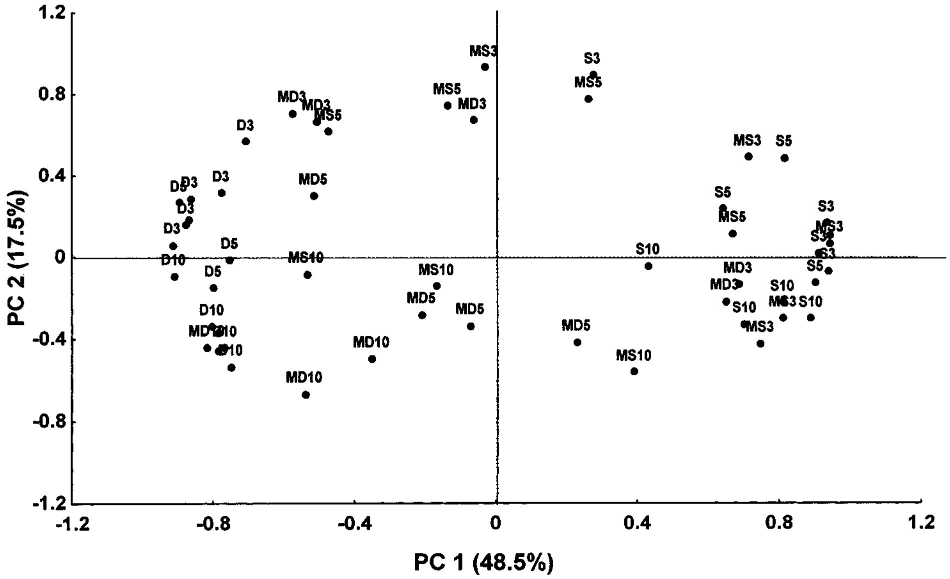

Figure 1. Extracted principal components as a function of 14 physicochemical variables for 52 samples of Madeira wine according to the type and age, projected in the plane defined by the first two PCs.

Table 3. Factor Loadings for the First Two PCs of a Test Set of Physicochemical Data from the 52 Samples of Madeira Wine

physicochem parameters	factor loadings	
	PC 1	PC 2
pH	−0.3852 29	0.329 420
tot. acidity	0.859 725	0.160 750
fix acidity	0.725 512	0.122 528
volatile acidity	0.897 531	0.228 154
tartaric acid	0.254 002	0.169 348
°alcoholic	0.389 671	0.313 144
tot. polyphenols	−0.115 086	0.500 714
tot. sugar	−0.403 456	0.878 832
nonreducing extract	0.586 944	0.572 034
tot. dry extract	−0.314 873	0.913 975
density	−0.330 602	0.894 425
°Baumé	−0.345 082	0.899 293
ash	0.594 089	0.281 642
ash alkalinity	0.496 469	−0.285 297
chlorides	0.777 298	0.164 332
phosphates	0.445 483	0.040 679
sulfates	0.667 697	0.283 227
SO_2 tot.	−0.107 297	0.606 433
SO_2 free	−0.052 654	0.274 037
5-HMF	0.272 816	0.501 307
methanol	0.621 599	0.124 077
ethanal	0.734 921	0.446 397
ethyl acetate	0.892 203	0.255 213
2-butanol	0.395 853	0.228 452
1-propanol	0.702 202	−0.217 053
2-methyl-1-propanol	0.838 922	−0.238 979
2-propene-1-ol	0.454 255	0.234 623
1-butanol	0.568 346	0.026 692
3-methyl-1-butanol + 2-methyl-1-butanol	0.820 000	−0.262 653
tot. higher alcohols	0.839 931	−0.231 536

clearly satisfactory separation of the 12 groups involved. It could be seen for all types that samples 5 years old, as expected, are clearly among samples 3 and 10 years old.

By the observation of Table 4, it could be concluded that the first discriminant function (root 1), as expected, provides a great contribution to the discrimination of the type or sweetness degree, where the main variables, *total sugar*, *total dry extract*, *density*, and °Baumé, showing negative coefficients, are heavily weighted. The second discriminant function (root 2) seems to be clearly

Table 4. Canonical Roots for the First Two Discriminant Functions of a Test Set of Physicochemical Data from 52 Samples of Madeira Wine

physicochem parameters	canonical roots	
	root 1	root 2
tot. acidity	0.069 984	0.423 990
fix acidity	0.059 815	0.288 456
volatile acidity	0.057 606	0.608 998
tot. sugar	−0.602 766	0.059 148
tot. dry extract	−0.651 603	0.175 920
density	−0.669 094	0.117 525
°Baumé	−0.738 791	0.136 907
chlorides	0.037 925	0.368 008
ethanal	−0.010 162	0.442 561
ethyl acetate	0.033 416	0.474 717
1-propanol	0.060 748	0.140 324
2-methyl-1-propanol	0.096 974	0.225 829
3-methyl-1-butanol + 2-methyl-1-butanol	0.091 527	0.201 173
tot. higher alcohols	0.089 612	0.217 312

related to aging, where *total acidity*, *volatile acidity*, *ethanal*, and *ethyl acetate* have the highest influence as can be demonstrated by the magnitude of the corresponding positive coefficients. In fact, such physicochemical parameters which showed such heavy weighting used to be considered the most important variables to characterize the wine samples, concerning the type and aging, respectively.

To organize such observed data into meaningful structures, those eight physicochemical variables should be sufficient for a correct description of the similarities among Madeira wine samples, according to type and age, as illustrated by the tree of hierarchical clustering of the Euclidean distances (dendrogram), as can be observed in Figure 3. The complete linkage hierarchical clustering clearly differentiates between medium sweet/medium dry and dry old samples and the other wines having different types and ages. Within each of these main clusters, the samples are correctly assigned to subclusters as sweet old, dry young, medium sweet young, medium dry young, and sweet young, where a clear differentiation could be observed. In the medium sweet young cluster, a very good differentiation could also be observed between samples 3 and 5 years old.

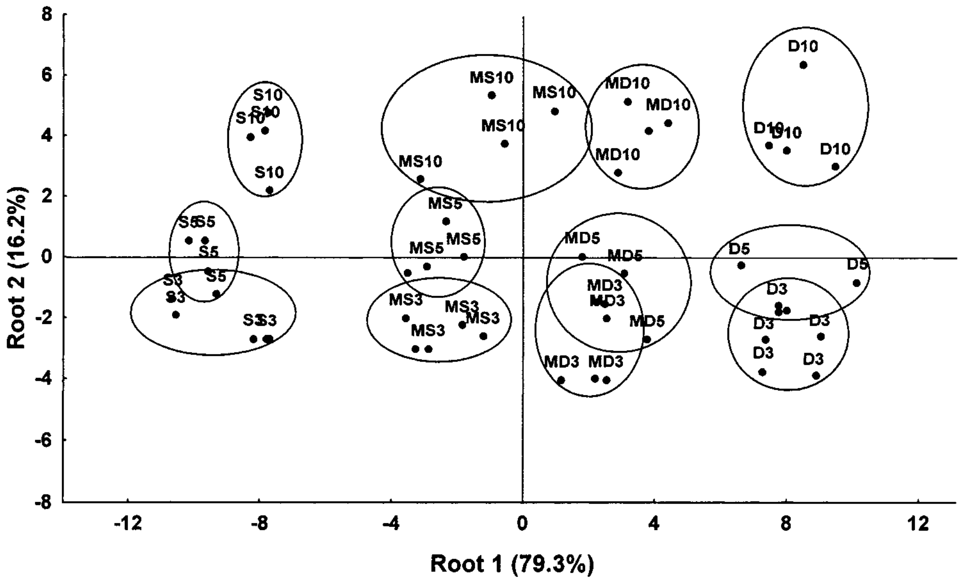

Figure 2. Scattered plot of 52 samples of Madeira wine, according to the type and aging, projected in the plane defined by the first two canonical discriminant functions from 14 physicochemical variables.

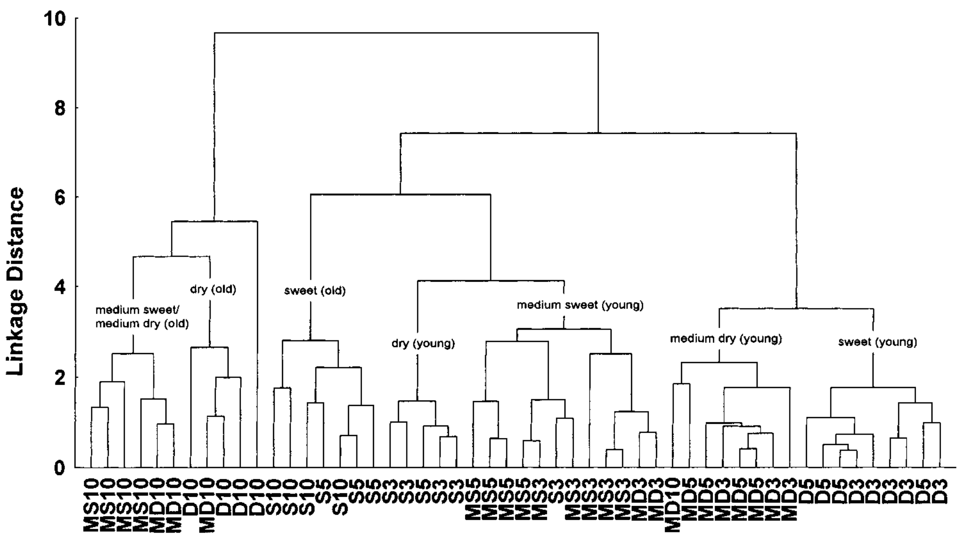

Figure 3. Complete linkage hierarchical clustering (dendrogram) for 52 samples of Madeira wine, through the measure of Euclidean distances, using physicochemical data: total acidity, volatile acidity, total sugar, total dry extract, density, °Baumé, ethanal, and ethyl acetate.

It can be also seen that several samples 5 years old could have either a younger or older behavior, which depends on the physicochemical characteristics more markedly, as shown by the sweet old, dry young, medium dry young, and sweet young clusters. Such observation could be supported especially by the two kind of aging processes implemented; baking conditions give a more hardy aging (older behavior) and the sun influence promotes a soft aging (younger behavior).

Sensorial Characterization. Table 5 shows the resume of the average data (mean ± SD) from sensorial analysis of Madeira wine samples, according to type and age, obtained by the council of tasters.

In the *sight* category, it could be seen that the average related the depth of color increase with the sweetness, which seems to be in agreement with the total polyphenols average content, observed in the physicochemical analysis, mainly responsible for the tonality of the wines. The average limpidity decreased with the age for all types, as expected, because the probability of turbidity occurrence increases much more with the aging process.

In the *smell* category, the average aroma intensity and quality seem to increase with aging for all types, and the strange aroma showed very low average values.

The *taste* category demonstrated that average sweetness increased with the type but clearly decreased with aging, as expected, which seems to be in agreement with the total sugar parameter observed in physicochemical analysis. The average acidity and bitter increased also with aging, and the first seems to be in agreement with the total acidity parameter observed also in physicochemical analysis. The taste quality, body, and finish seem to increase both with the type and aging. Very low values for strange tastes are present, and the tipicity shows substantial global appreciation, for which the older samples are a good examples.

Such considerations are the direct observation of sensorial data in Table 5 clearly present great difficulty for establishing criteria interpretation concerning the

Table 5. Resume of the Average Data Obtained from Sensorial Analysis of Madeira Wine Samples, According to the Type and Age

TYPE	Dry			Medium Dry			Medium Sweet			Sweet		
AGE (years) ⇨	3	5	10	3	5	10	3	5	10	3	5	10
TASTER (%)*												
Sight												
depth of colour	55.83±15.27	52.08±12.95	64.59±7.59	69.32±15.48	60.62±11.73	75.42±9.19	78.00±5.73	81.88±2.99	76.88±11.33	79.87±8.35	80.83±3.97	73.75±7.77
limpidity	60.33±9.80	62.38±5.94	51.87±10.87	59.00±5.32	52.92±8.29	44.00±10.14	58.99±13.02	61.04±2.29	52.92±10.51	55.66±23.77	67.50±4.03	57.08±17.66
Smell												
intensity	59.33±6.86	60.42±5.99	63.75±3.70	56.17±3.21	54.38±4.32	65.42±10.31	56.33±1.73	58.96±3.62	58.96±2.75	55.03±3.64	63.33±4.46	64.79±5.42
aroma quality	52.50±6.87	56.50±7.96	53.13±11.81	51.50±2.31	48.75±4.38	63.54±12.27	53.84±5.55	60.21±3.93	56.88±5.95	51.33±5.19	6.00±4.95	60.21±7.21
strange aromas	12.83±6.73	9.00±4.72	11.67±6.45	11.67±5.00	7.50±4.30	8.71±7.52	8.17±2.79	8.75±3.44	4.79±0.80	11.24±0.12	5.42±3.08	6.88±1.85
Taste												
sweetness	41.50±5.57	45.83±4.91	32.71±8.54	63.33±6.24	53.54±5.42	51.04±6.50	74.00±3.35	72.71±2.19	61.88±12.66	79.17±4.89	79.59±3.23	71.25±4.33
acidity	28.00±4.19	28.96±5.54	32.71±1.72	26.17±3.80	32.50±3.60	30.83±5.05	27.20±2.46	28.54±0.80	33.13±1.42	29.33±3.14	25.42±2.10	31.25±0.83
bitter	32.33±3.60	28.33±2.89	29.17±11.30	21.73±4.75	23.96±5.11	26.67±5.53	24.16±7.75	24.17±6.27	29.79±2.84	25.33±4.62	18.96±4.32	26.88±5.82
taste quality	48.33±2.43	53.34±10.74	50.42±10.49	52.83±4.11	55.62±5.02	55.42±8.40	55.17±5.85	55.63±5.20	61.25±7.25	53.13±5.83	61.67±5.05	61.25±5.29
body	47.17±3.66	55.84±8.63	54.38±7.21	54.17±5.43	52.08±4.54	53.13±7.50	57.33±3.70	59.17±3.60	58.33±3.91	56.33±4.43	60.63±1.25	61.46±3.36
finish	51.83±7.20	54.58±12.07	58.75±12.35	56.50±4.46	55.21±2.19	62.29±7.21	61.33±3.75	56.67±5.57	61.04±2.49	59.33±5.38	60.63±5.95	65.42±1.60
strange tastes	9.57±3.40	9.79±6.06	8.13±4.78	9.80±5.51	6.96±4.94	9.79±1.58	5.32±4.02	7.71±1.72	3.67±1.13	8.16±2.16	4.17±1.18	7.25±1.66
Global Appreciation												
tipicity	59.83±2.24	61.04±10.24	61.25±7.02	58.68±2.17	60.42±2.20	63.29±4.20	61.07±4.96	61.04±3.87	63.96±3.99	57.89±6.20	65.00±3.26	64.42±5.60

*: Mean ± Standard Deviation

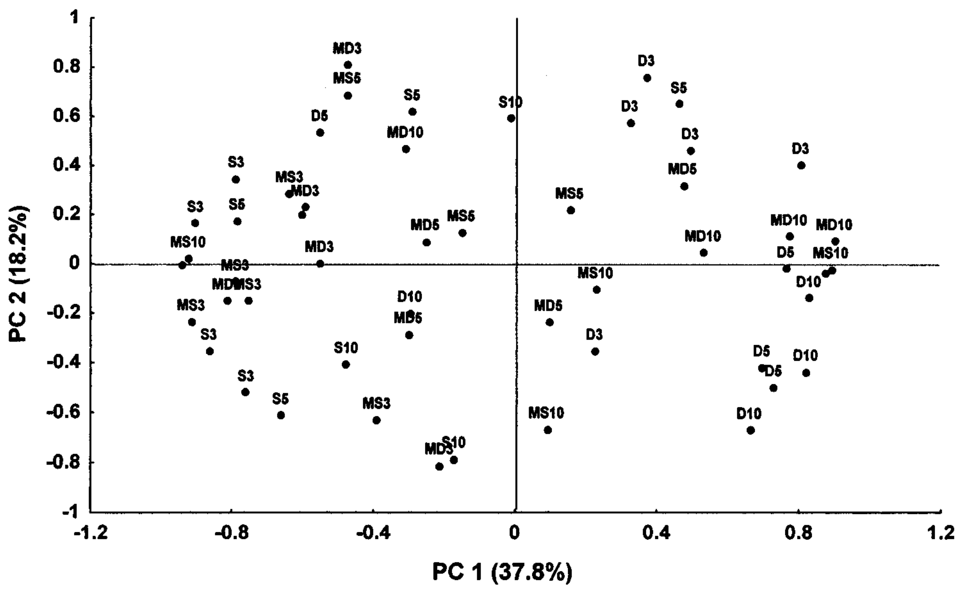

Figure 4. Extracted principal components as a function of six sensorial variables from the 52 samples of Madeira wine according to the type and age, projected in the plane defined by the first two PCs.

differentiation and similarities between the samples, which for such purpose multivariate analysis was also employed.

The first PCA approach indicates that the first two PCs explain 58% of the variability among the samples studied. The observation of the loading scores in Table 6 suggests that six sensorial variables, having the coefficient magnitudes higher that 0.70, may be enough to adequately describe the samples according to age, as *aroma quality*, *taste quality*, *body*, *finish*, and *tipicity*, shown in the PC 1. According to the type, *sweetness* can adequately describe the samples as shown in the PC 2.

In Figure 4 can be seen the scores plot extracted from the first two PCs derived from a data set of the six variables measured on 52 samples, which now explain 56% of the variability contained in both vectors. Indeed, the PC 1 axis seems to be responsible for some differentiation between sweet and dry samples and the PC 2 axis shows clearly a very low differentiation among young and old samples.

Table 6. Factor Loadings for the First Two PCs of a Test Set of Sensorial Data from the 52 Samples of Madeira Wine

	factor loadings	
sensorial parameters	PC 1	PC 2
depth of color	−0.556 945	0.419 354
limpidity	−0.054 760	0.322 587
aroma intensity	−0.600 511	−0.549 580
aroma quality	−0.852 954	−0.255 250
strange aromas	0.685 113	−0.013 666
sweetness	−0.403 622	0.783 023
acidity	−0.182 606	−0.657 275
bitter	0.285 493	−0.540 243
taste quality	−0.913 704	0.019 656
body	−0.869 093	0.097 604
finish	−0.829 290	−0.146 269
strange tastes	0.576 034	−0.232 341
tipicity	−0.837 898	−0.212 940

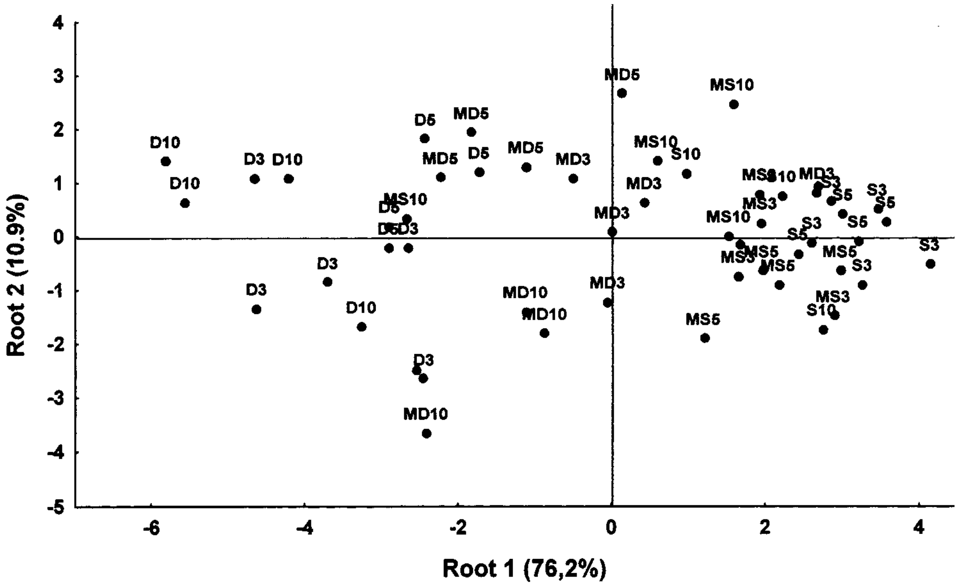

Figure 5. Scattered plot of 52 samples of Madeira wine, according to the type and aging, projected in the plane defined by the first two canonical discriminant functions from six sensorial variables.

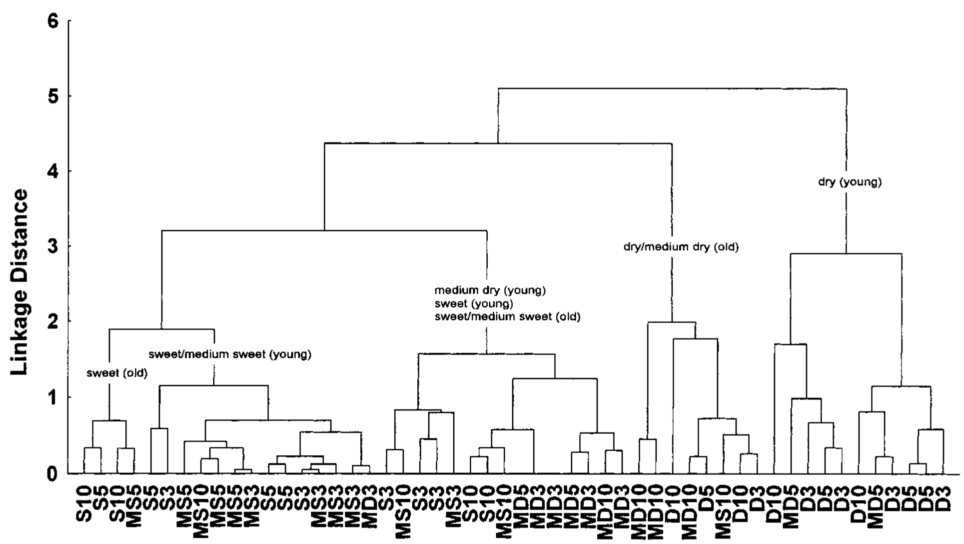

Figure 6. Complete linkage hierarchical clustering (dendrogram) for 52 samples of Madeira wine, through the measure of Euclidean distances, using sensorial data; sweetness and aroma quality.

Table 7. Canonical Roots for the First Two Discriminant Functions of a Test Set of Sensorial Data from 52 Samples of Madeira Wine

sensorial parameters	canonical roots	
	root 1	root 2
aroma quality	0.052476	−0.392235
sweetness	0.937895	−0.044620
taste quality	0.142456	0.120643
body	0.212100	0.107663
finish	0.109634	−0.086556
tipicity	0.013668	−0.034706

Canonical analysis was used again to determine which sensorial variables better discriminate between the type and age groups; shown in Figure 5 is the scatterplot of canonical scores for the first two discriminant functions (root 1 and root 2), which explains 87.1% of the variability, where can be seen a very low separation of the 12 groups involved. By the observation of Table 7, it could be concluded that the first discriminant function (root 1) is more related to the type, where the *sweetness* variable is heavily weighted, as was expected. The second discriminant function (root 2) seems to be more related to aging, where *aroma quality* has the highest influence, as can be demonstrated by the magnitude of the corresponding coefficient.

By using such two sensorial parameters for a description of the similarities among Madeira wine samples, according to type and age, Figure 6 illustrates the tree of hierarchical clustering of the Euclidean distances (dendrogram). The complete linkage method of hierarchical clustering could differentiate between groups in the majority constituted by similar samples as dry young and the other wines having different types and ages. Within each of these main clusters, the samples are assigned to subclusters as dry/medium dry old, sweet/medium sweet young, and sweet old and a cluster having a mixing of medium dry young, sweet young, and sweet/medium sweet old samples, where a low differentiation could be observed. It could be also seen that the medium sweet samples 10 years old are completely scattered all over the dendrogram.

The explanation of such a low differentiation could be supported by Madeira winegrowing, especially the aging conditions and chemical corrections implemented. Such practice obviously influenced very much the organoleptic analysis, always of high subjectivity, made by the council of tasters.

CONCLUSIONS

The main physicochemical and sensorial parameters were used to characterize Madeira wine commercially available in the market, according to standard methodology and European Union regulation.

The physicochemical data obtained from the 52 samples of Madeira wine, having different type and ages, representative of the delimited region of Madeira (*vlqprd*), showed values in general clearly below the maximum concentration admissible by the national and/or international rules. Such characterization is an important reference for Madeira wine commercially available as an aperitif and/or dessert liquor of high quality.

Principal component analysis from the physicochemical data indicates that 14 variables may be enough to explain 66% of the variability among samples, where a very good differentiation is observed, concerning the type and aging groups. Canonical analysis confirms that eight physicochemical variables are enough to discriminate between type and aging, as *total sugar*, *total dry extract*, *density*, and °Baumé and *total acidity*, *volatile acidity*, *ethanal*, and *ethyl acetate*, respectively. The complete linkage hierarchical clustering clearly differentiates the samples studied between medium sweet/medium dry old, dry old, sweet old, dry young, medium sweet young, medium dry young, and sweet young.

Sensorial characterization showed results of some difficult interpretation, but in general substantial depth of color, limpidity, and aroma quality were observed, where the medium sweet and sweet old samples were accorded the highest appreciation by the council of tasters.

Principal component analysis of sensorial data indicates that six variables may be enough to explain 56% of the variability among samples, where a poor differentiation could be observed, especially concerning the aging. Canonical analysis confirms that two sensorial variables load to high, *sweetness* and *aroma quality*, but only a low discrimination is observed especially for the type group. The hierarchical clustering shows a very low differentiation between grouping in the majority constituted by similar samples as dry young, dry/medium dry old, sweet/medium sweet young, and sweet old and a cluster having a mixing of samples as medium dry young, sweet young, and sweet/medium sweet old.

In general, Madeira wine differentiation seems to be more controlled especially by exogenous factors, due the aging conditions and chemical corrections implemented, during the winegrowing process.

ACKNOWLEDGMENT

We thank the Madeira Wine Institute, including their council of tasters that made the sensorial analysis and João Abel da Silva Santos for supplying the wine samples, Laboratório Agrícola da Madeira for all technical assistance given, in particular Paulo Jorge Pestana Fernandes for the execution of the residue analysis, and Marco Gomes da Silva (FCT/UNL) for his help in the multivariate data analysis.

LITERATURE CITED

Brazão, J.; Laureano, O.; Influência da Estufagem nas Caracteristicas Físico-Químicas e Organolépticas de "Vinho da Madeira". *3rd Symp. Vitic.* **1995**, *2*, 117−130 (in Alentejo, Évora, Portugal).

Cabais, J. C.; Cooper, J. F. *Résidus de Produits Phytosanitaires das les Vins-Approches Toxicologiques et Analytiques*, RF OE, No. 130, 1991.

EU Regulation: *Common Organization of Vinegrowing Market*, No. 822, Mar 16, 1987.

EU Regulation: *Special Dispositions Related with Quality Wines Produced in Delimited Regions*, No. 823, Mar 16, 1987.

EU Regulation: *Commercialization of Liquors Wines Produced in European Community*, No. 4252, Dec 21, 1988.

EU Regulation: *Liquors Wines Quality Produced in Delimited Regions*, No. 3111, Nov 10, 1993.

Ferreira, M. A.; Fernandes, J. O. The application of an improved GC-MS procedure to investigate ethyl carbamate behavior during the production of Madeira wines. *Am. J. Enol. Vitic.* **1992**, *43* (4), 339−343.

Freitas, A. M. F. *Perfil de Aminoácidos Livres como Parâmetro Enológico para Caracterização de Vinhos Elementares Alentejanos em Função da Casta de* Origem. Ph.D. Thesis, Évora, Portugal, 1988.

Garcia, A. S. C. *Controle de Qualidade dos Vinhos*; Inst. da Vinha e do Vinho: Lisboa, Portugal, 1988.

Garcia, J. C. M.; Garcia, M. M. S.; Carro, M. N.; Torrijos, R. C. GC-MS Identification of Some Wine Aroma Compounds in Galician White Wines. *Proc. 18th Int. Symp. Capillary Chromatogr.* **1996**, *2*, 621−631 (Riva del Garda, Italy, Hüting).

Guide Concernant les Recomendations du Codex se Repportant aux Résidus de Pesticides, partie 7, Directives du Codex Concernant les Bonnes Pratiques en Matiére d'Analyse des Pesticides, FAO7OMS, CAC7PR7, Rome, 1985.

Hair, J. F., Jr.; Anderson, R. E.; Tatham, R. L.; Black, W. C. *Multivariate Data Analysis*, 4th ed.; Prentice Hall International Inc.: Englewood Cliffs, NJ, 1995.

Jornal Oficial da Madeira, P. 80/94, I Série, No. 10, April 15, 1982.

Jornal Oficial da Madeira, P. 16/94, I Série, No. 29, Mar 18, 1994.

Livingstone, D. *Data Analysis for Chemists*; Oxford Sci. Pub.: New York, 1995.

Lopes, L. *Madeira-Um Vinho Singular*; Rev. de Vinhos, 57, 1994.

Manly, B. F. J. *Multivariate Statistical Methods*, Chapman & Hall: London, 1997.

Martins, J. P. *Vinhos de Portugal: notas de prova*; Pub. D. Quixote: Lisboa, Portugal, 1998.

Noble, A. C., Flath, R. A., Forrey, R. R., Wine headspace analysis. Reproducibility and application to varietal classification. *J. Agr. Food Chem.* **1980**, *28* (2), 346−353.

Nogueira, J. M. F.; Nascimento, A. M. D. Higher Alcohol's in Madeira Wine. *Proc. 18th Int. Symp. Capillary Chromatogr.* **1996**, *2*, 1162−68 (Riva del Garda, Italy, Hüting).

Nogueira, J. M. F.; Nascimento, A. M. D. Análise Comparativa do Vinho da Madeira. *Proc. 3rd Meet. Mediterranean Food Chem.* **1997**, 132−134 (SPQ, Faro, Portugal).

NP 2139, Determination of Total Acidity Content; IPQ: Lisboa, Portugal, 1987.

NP 2140, Determination of Volatile Acidity Content; IPQ: Lisboa, Portugal, 1987.

NP 2141, Determination of Fix Acidity Content; IPQ: Lisboa, Portugal, 1987.

NP 2142, Determination of Relative Density; IPQ: Lisboa, Portugal, 1986.

NP 2143, Determination of Alcoholic Volumetric Content; IPQ: Lisboa, Portugal, 1987.

NP 2220, Determination of Free, Combined and Total Sulfur Dioxide Content; IPQ: Lisboa, Portugal, 1987.

NP 2221, *Determination of Ash*; IPQ: Lisboa, Portugal, 1987.
NP 2222, *Determination of Total Dry Content*; IPQ: Lisboa, Portugal, 1987.
NP 2226, *Determination of Chlorides Content, Potentiometric Method*; IPQ: Lisboa, Portugal, 1988.
NP 2227, *Determination of Sulfates Content*; IPQ: Lisboa, Portugal, 1988.
NP 2228, *Determination of Non Reducing Extracted Content*; IPQ: Lisboa, Portugal, 1988.
NP 2279, *Determination of Ash Alkalinity*; IPQ: Lisboa, Portugal, 1988.
NP 3263, *Determination of Ethanal, Ethyl Acetate, Methanol, 2-Butanol, 1-Propanol, 2-Methyl-1-Propanol, 2-Propene-1-ol, 1-Butanol, 2-Methyl-1-Butanol + 3-Methyl-1-Butanol*; IPQ: Lisboa, Portugal, 1990.
NP 3381, *Determination of 5-Hydroxymethylfurfural*; IPQ: Lisboa, Portugal, 1990.
Recueil des Méthodes Internationales d'Analyse des Vins et des Moûts; OIV: Paris, 1990.
Read, J. *Vinhos de Portugal*. *Círculo Leitores*, **1995**, *3*.
Ribéreau-Gayon, J.; Peynaud, E.; Sudraud, P.; Ribérea-Gayon, P. *Traitê d'Oenologie- Sciences et Techniques du Vin (Analyse et Controle des Vins)*; Dunod: Paris, 1982.
Rossi, I. A.; Clyne, A. H.; Fox, A. P.; Walker, D. A. Analytical strategies to confirm Scotch whisky authenticity. *Analyst* **1994**, *119*, 1741−1746.
Vasconcelos, A. M. P.; Chaves das Neves, H. Characterization of elementary wines of *Vitis vinifera* by pattern recognition of free amino acid profiles. *J. Agr. Food Chem*. **1989**, *37* (4), 931−937.
Vasconcelos, A. M. P.; Chaves das Neves, H. HRGC of wine free amino acids as a tool for elementary wine characterisation. *J. High Resolut. Chromatogr*. **1990**, *13*, 494−498.
Vieira, A. *Breviário da Vinha e do Vinho na Madeira*, Eurosigno Pub., 2nd ed.; Açores, Portugal, 1991.

Received for review May 4, 1998. Revised manuscript received October 30, 1998. Accepted November 2, 1998. We thank Programs PRODEP for financial support.

JF9804490