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ATTEMPT TO CLASSIFY THE YERBA MATE ACCORDING TO THE COUNTRY OF ORIGIN BASED ON COLOR PARAMETERS

PRÓBA KLASYFIKACJI YERBA MATE WEDŁUG KRAJU POCHODZENIA NA PODSTAWIE PARAMETRÓW BARWY

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Abstract: Infusions prepared from yerba mate are good sources of antioxidants, especially polyphenols in the diet. The aim of this work is to evaluate the color parameters of the yerba mate leaves in order to identify the samples of yerba mate grown and processed in different regions of Argentina, Brazil and Paraguay. Significant differences were observed for most color parameters, indicating the possibility to classify the yerba mate samples by statistical analysis. The results indicated that the country of origin, as well as the brand, among Argentinian samples of yerba mate had a significant effect on color parameters (CIEL*a*b*). However, the most significant differences were detected between yerba mate from Brazil and samples from other countries.

Keywords: yerba mate, color parameters, identification.

Streszczenie: Napary yerba mate są bogatym źródłem antyoksydantów, w tym szczególnie związków polifenolowych, które decydują o ich walorach zdrowotnych i sensorycznych. Obecność tych związków wpływa również na barwę naparu, która jest bardzo istotnym czynnikiem decydującym o wyborze danego produktu. Celem artykułu był pomiar barwy naparów yerba mate i wykorzystanie oznaczonych parametrów do różnicowania yerba mate pochodzących z różnych krajów (Argentyny, Brazylii i Paragwaju). Uzyskane rezultaty wskazywały na możliwość wykorzystania parametrów barwy do różnicowania badanych produktów. Analizując uzyskane wyniki, stwierdzono statystycznie istotny wpływ kraju pochodzenia, jak również marki dla naparów pochodzących z Argentyny na parametry barwy. Najsilniejsze różnice stwierdzono pomiędzy próbami pochodzącymi z Brazylii i innych krajów.

Słowa kluczowe: yerba mate, parametry barwy, identyfikacja.

1. INTRODUCTION

Yerba mate (*Ilex paraguariensis* A. St. Hil.) is a native plant in subtropical regions in South America. Infusions of powder of yerba mate leaves are widely consumed, mainly as chimarrão or mate (warm or hot) and tererê (cold) in Argentina, southern of Brazil, Paraguay and Uruguay [Marcelo et al. 2014]. Aqueous extract of yerba mate is an antioxidant-containing beverage largely consumed in several South American countries, such as Uruguay, Argentina, Brazil, and Paraguay. The yerba mate beverage is prepared as a hot infusion of the dried and minced leaves of yerba mate and is much appreciated for its herbal, tobacco flavors, bitter and astringent taste [Dmowski and Kłopotek 2016] and stimulating and antioxidant properties [Boaventura et al. 2015; Cardozo and Morand 2016]. The traditional habit to drink this beverage is historically connected with native people from Brazil, Paraguay and Argentina, and particularly the Guarani ethnicity. Among Guarani people, the plant is known as caá (herb) while the infusion as caá-i (herb water). Jesuit priests (1610–1768) described the use of this beverage as the main foodstuff among the Guarani, with intensive trade among tribes from Brazil, Bolivia, Peru, and Chile. Eventually the habit of drinking mate spread among the Portuguese colonizers, and plantations and a trade network were established by the Jesuits to meet this demand [Linck, Manzali de Sá and Elisabetsky 2015].

Yerba mate leaves contain high concentrations of phenolic compounds, mainly tannins, flavonoids and phenolic acids, which provide a significant amount of antioxidants to the herb, decreasing the oxidation of human low density lipoprotein (LDL) either in vitro or in vivo [Frizon et al. 2015]. Caffeine (1,3,7-trimethylxanthine) one of methylxanthines found in highest concentration in yerba mate [Pawlak-Lemańska et al. 2016; Rój, Przybyłowski and Pietrusińska 2016], presents a stimulating action to the central nervous system and can increase the use of fat as an energy source. Its therapeutic properties are numerous and can act on the circulation, renal function and in better coordination of brain functions and, consequently, an increase of alertness and mental activity [Anesini et al. 2012; Gonzalez de Mejia et al. 2016]. In recent research [Pawlak-Lemańska et al. 2016] it was found that yerba mate infusions are good sources of antioxidants, especially polyphenols in the diet. There was also found that teas are more rich source of polyphenols than yerba mate, but for one portion of yerba mate infusion, two or three times more dry leaves is usually used than for tea infusion. Therefore, the intake of polyphenols is the same or even higher than after drinking one cup of black or green tea.

Food products (also yerba mate) are usually related to their place of origin, which has become increasingly important, bearing in mind the increased interest for food with clear quality and origin [Luykx and van Ruth 2008]. Producers directly associate the brand with the product provenance in order to obtain market recognition, better prices and other commercial advantages. In conjunction with

regulatory authorities, producers have interest in ensuring correct labeling of their product as well as methodologies for authentication. To this end, different techniques and multivariate analysis have been used [Marcelo et al. 2014]. The heating process (drying and/or roasting), to which the mate leaves are subjected before consumption, leads to a large amount of products degradation and enhances color. As it occurs in other beverages like tea, the carotenoid degradation yields different norisoprenoids; these kinds of compounds are desirable because they give sophisticated color notes [Márquez et al. 2013]. The concentrations of tannins and other polyphenol compounds in the leaves and water temperature may influence the extraction of the elements and consequently the concentration of the color parameters in the yerba mate infusion.

Color of foods is the first contact point of the consumer with it, so it strongly influences consumers' preferences. Color has a major role in the acceptability of the product and is related to the consumer perception of flavor, sweetness, scents and other physical properties in relation to the quality of the product. Consumer choice depends on the quality of the product, the color has such a psychological impact on the consumer that it is directly associated to the quality of the product. Color is one of the main parameters of the quality of for example: ceramics and wine especially of red ones. In wineries, the routine analyses of the color in wines are made to control and evaluate the wine quality [Pérez-Magariño and González-Sanjosé 2013]. The color provides information about defects, the type, and also has an important influence on the overall acceptability by consumers. Thus, the implementation of instrumental measurements of color for the quality control is correlated to the consumer choice [Heras-Roger, Díaz-Romero and Darias-Martín 2016; Rój, Przybyłowski and Pietrusińska 2016].

The classification of food samples is of great interest for identification of the product's geographical origin and authenticity, or for establishing characteristics of products. In the case of yerba mate some classification studies have been carried out based on atomic spectroscopy measurements, but these methods are expensive [Marcelo et al. 2014]. The main objective of this work is to propose a simple and cheap methodology to differentiate yerba mate obtained from the Tri-city market. By considering the hypothesis that some differences can occur between colors of samples from different regions of origin, models based on CIEL*a*b* coordinates of yerba mate have been developed. According to a recent survey of literature, to date no many research has been reported using color parameters (CIEL*a*b*) for the determination of country of origin of the yerba mate, which is relevant considering that this analysis can be inserted into the trade market allowing important conclusions about the country of origin of mate leaves. It could be very useful for producers and first of all for consumers, to identify the good quality of yerba mate. Within this context, the aim of this work is to evaluate the color parameters the leaves of yerba mate in order to identify the samples of yerba mate

(*I. paraguariensis*) grown and processed in different regions of Argentina, Brazil and Paraguay.

2. MATERIAL AND METHODS

The samples of yerba mate tea were obtained from the Tri-city market. The samples originated from three countries and from eight producers: from Argentina – Taragui (A_Tar), Rosamonte (A_Ros), Amanda (A_Am), Union Bio (A_UnBio) and Taragui sin palo (A_Tsp), from Paraguay – Pajarito (P_Paj) and Colon (P_Col) and from Brazil – Green Despalada (B_GrDe).

2.1. Determination of the color in yerba mate samples

Several systems for expressing color numerically were developed by an international organization concerned with issues of lighting and color, the International Commission on Illumination (CIE). One of the best known of these systems is the Lab color space (also referred to as CIEL*a*b*) devised in 1976. The principle of colorimetry is based on the tristimulus method, i.e., each color is the combination in different proportions of red, green and blue. For one color, the colorimeter gives the percentages of the three primary colors. A set of three sensors filtered to have nearly the same color sensitivity as the human eye, receive light from the object and transmit the information to the data processor that determines the tristimulus values XYZ by the standards of the CIE. In this space L* indicates lightness, its value extended from 0 (black) to 100 (white). a* and b* are the chromaticity coordinates. The a* and b* indicate color directions: +a* is the red direction, -a* is the green direction, +b* is the yellow direction, and -b* is the blue direction. The center is achromatic, as the a* and b* values increase and the point moves out from the center, the saturation of the color increases [Korifi et al. 2013].

The color parameters of yerba mate leaves were determined with a Konica Minolta CR-400 colorimeter. All samples of yerba mate should have the same form; therefore, leaf teas were ground in a mortar. The determination was performed in the CIE system, which is based on measuring the three trichromatic components (L*, a*, b*). The total color difference (ΔE^*) between two samples were obtained using the following expression: $\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ in CIEL*a*b* units. All the parameters were measured twice in every sample. Samples of yerba mate tea were obtained from the Tri-city market. The samples originated from three countries and from eight producers: from Argentina – Taragui (A_Tar), Rosamonte (A_Ros), Amanda (A_Am), Union Bio (A_UnBio) and Taragui sin palo (A_Tsp), from Paraguay – Pajarito (P_Paj) and Colon (P_Col) and from Brazil – Green Despalada (B_GrDe).

2.2. Statistical analysis

Statistical analysis of the results included the calculation of basic measures such as the mean value. Significance of the different brand of yerba mate was determined using STATISTICATM12. A one-way analysis of variance (ANOVA) and Kruskal-Wallis were performed for testing significant group differences followed by a post hoc Tukey's (HSD) test, to determine which groups differed significantly. Differences were considered statistically significant when $P \leq 0.05$. Principal component analysis (PCA) was used to discriminate between varieties. PCA using the correlation matrix was conducted using STATISTICATM12 to visualize and elucidate the relationships between the samples. Agglomerative hierarchical clustering (AHC) was also performed to identify the relationships between test samples. A dendrogram of AHC was used to visually present information regarding clustering based on dissimilarity between yerba mate samples.

3. RESULTS AND DISCUSSION

The mean and statistic data of color parameters concentrations determined in the 48 samples of yerba mate are shown in Table 1.

Table 1. Mean values of attributes (color units CIEL*a*b*) for some selected yerba mate of the different regions origin

Tabela 1. Średnie wartości parametrów dla badanych próbek yerba mate pochodzących z różnych rejonów

| Country of origin/brand | Argentina | | | | | Paraguay | | Brazil |
|-------------------------|---------------------------------|---------------------|-------------------|---------------------|---------------------|---------------------|---------------------|-------------------|
| | A_Tar | A_Ros | A_UnBio | A_Am | A_Tsp | P_Paj | P_Col | B_GrDe |
| L* | 57.2 ^{a,b} | 54.6 ^{a,b} | 59.3 ^b | 52.4 ^{a,c} | 52.2 ^{a,c} | 56.1 ^{a,b} | 55.1 ^{a,b} | 47.9 ^c |
| ANOVA test | F(7,48) = 5.93; p = 0.00009 | | | | | | | |
| K-W test | KW-H(7;88) = 41.71; p = 0.0000 | | | | | | | |
| a* | -0.6 ^a | -0.6 ^a | -0.8 ^b | -0.6 ^{a,b} | -0.5 ^a | -0.5 ^a | -0.2 ^d | -1.9 ^c |
| ANOVA test | F(7,48) = 75.28; p = 0.00000 | | | | | | | |
| K-W test | KW-H(7;88) = 40.27; p = 0.00000 | | | | | | | |
| b* | 15.7 ^b | 15.2 ^a | 15.2 ^a | 16.2 ^{b,c} | 16.4 ^c | 17.1 ^d | 18.1 ^e | 15.2 ^a |
| ANOVA test | F(7,48) = 112.57; p = 0.00000 | | | | | | | |
| K-W test | KW-H(7;88) = 43.20; p = 0.00000 | | | | | | | |

Source: own study.

As can be seen in Table 1, the mean parameter L^* was higher for the Paraguay samples, it ranged from 55.08 (P_Col) to 56.07 (P_Paj), demonstrating a high whitening value, as expected since L^* represents lightness. The samples from Argentina showed high mean values of L^* - from 52.15 (A_Tsp) to 59.32 (A_UnBio) that are lower than the values obtained for the Paraguayan samples, but higher than those found for the Brazilian samples. The B_GrDe samples from Brazil showed the lowest values of L^* .

We can also note that the samples from Paraguay showed high values of the parameters a^* (-0.20 and -0.45 for P_Col and P_Paj respectively) and b^* (18.06 and 17.1 for P_Col and P_Paj respectively) demonstrating a loss of green and blue colors, and presenting a color closer to yellow. On the other hand, the Brazilian samples has lower a^* (-1.76) and b^* (15.20) values than the other samples, which makes this class closer to green.

The analysis of variance (ANOVA), Kruskal-Wallis analysis and post hoc Tukey's test were applied in order to determine whether the samples were different concerning the country. Significant differences (confidence level of 95%) were observed for most color parameters, indicating the possibility to classify the yerba mate samples by statistical analysis.

The results indicated that the country of origin, as well as the brand, among Argentinian samples of yerba mate had a significant effect on color parameters (CIEL*a*b*). However, the most significant effect was detected between yerba mate from Brazil and samples from other countries (Tab.1).

Our data are very similar to data presented by Rój et al. [2016]. They did not found significant differences ($p = 0.05$) for color parameters (CIEL*a*b*) of yerba mate beverages from Argentina and Paraguay.

Additionally, to study the color differences between samples from different region (countries) of origin, in CIELAB units, the ΔE^* parameters were calculated (Tab. 2).

Table 2. ΔE^* parameter for selected yerba mate samples
Tabela 2. Wartości parametru ΔE^* dla badanych próbek yerba mate

| | A_Tar | A_Ros | A_UnBio | A_Am | A_Tsp | P_Paj | P_Col | B_GrDe |
|---------|-------|-------|---------|------|-------|-------|-------|--------|
| A_Tar | - | 2.69 | 2.19 | 4.87 | 5.11 | 1.78 | 3.18 | 9.42 |
| A_Ros | | - | 4.76 | 2.40 | 2.70 | 2.40 | 2.91 | 6.80 |
| A_UnBio | | | - | 7.03 | 7.28 | 3.79 | 5.16 | 11.48 |
| A_Am | | | | - | 0.35 | 3.83 | 3.35 | 4.72 |
| A_Tsp | | | | | - | 3.98 | 3.38 | 4.61 |
| P_Paj | | | | | | - | 1.41 | 8.50 |
| P_Col | | | | | | | - | 7.90 |
| B_GrDe | | | | | | | | - |

Source: own study.

In general, the eye is able to discriminate two colors when $\Delta E^* \geq 1$, but when the untrained testers observe the products (such as yerba mate), the color discrimination is worse, decreasing the eye capacity to discriminate colors corresponding to ΔE^* up to five units [Pérez-Magariño and González-Sanjosed 2013]. Moreover, when ΔE^* is up to five units, it could indicate a significant differences, in color parameters, between the compared products. Average color differences of $\Delta E^* = 4.6$ for all samples and about $\Delta E^* = 4.0$ only for samples from Argentina were found in this study, including yerba mate used in the models and the predicted ones. Therefore, these results can be considered quite acceptable, since the color differences were more than five ΔE^* units in 30% of total yerba mate samples, and no yerba mate had color difference under two ΔE^* units (Tab. 2), except for differences between the individual samples of yerba mate from Paraguay and Argentina, where the ΔE^* parameters was not upper than two units (A_Tar-P_Paj; $\Delta E^* = 1.78$). By analyzing Table 2, we can see also that differences, between samples of yerba mate from Argentina, are not over than 3.00, except for differences between samples A_UnBio, A_Am, A_Tsp and T_Tar, where the differences are over five: A_UnBio-A_Am ($\Delta E^* = 7.03$); A_UnBio-A_Tsp ($\Delta E^* = 7.28$) and A_Tsp-A_Tar ($\Delta E^* = 5.11$) respectively. As can be seen, the samples from Argentina are very similar, despite of the fact that importers declare various areas of cultivation. The same situation we can see between samples from Paraguay. The Paraguay samples showed the low values of ΔE^* (1.41) that are lower than the values obtained for the other samples. The highest values of the ΔE^* parameters we can see between samples from Brazil and other countries. The mean value of ΔE^* parameters is 7.40 and 8.20 between Brazilian and Argentinian and Brazilian and Paraguayan samples respectively. By comparing the ΔE^* parameters, it was observed that samples from Argentina and Paraguay are coherent. The samples originated from Argentina are also coherent between each other.

Moreover, based on the results obtained and the dependencies existing between them, we can group the different brands of yerba mate (Fig. 1). The biplot drawn by the PCA provided visual information regarding the distribution of the eight yerba mate samples.

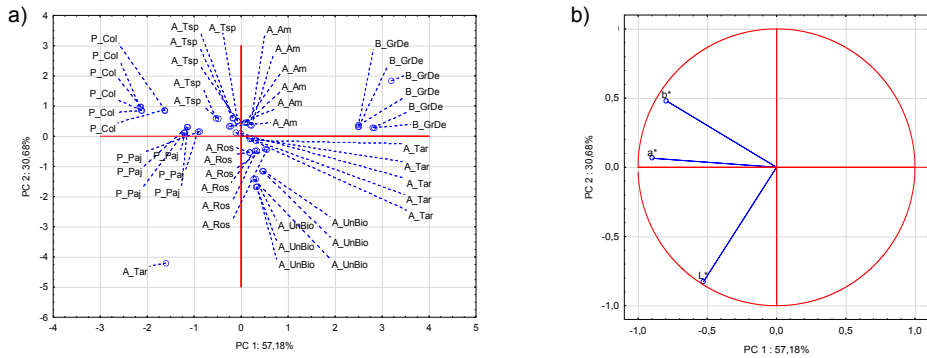


Fig. 1. Scores (a) and loadings (b) of the two first principal components (PCs), for the color parameters CIEL*a*b*. A-Argentina, B-Brazil and P-Paraguay

Rys. 1. Punkty (a) i ładunki (b) dwóch pierwszych składowych głównych (PCs) dla parametru barwy. A-Argentyzna, B-Brazylia i P-Paragwaj

Source: own study.

A total of 87.86% of the variance was described by three principal components (PC) drawn from the PCA. Specifically, 87.86% of the variance was explained by PC 1 and PC 2. PC1, with 57.18% of variance, separates most of the Brazilian samples of those from Paraguay. Brazilian samples are characterized by a lower value of L* parameter (these parameters are responsible for the negative part of PC2), a* and b* (these two elements are responsible for the positive part of PC2). On the other hand, L* parameter is higher in samples from Argentina and Paraguay and separates Brazil from the other countries. Argentine samples are characterized by higher concentrations of yellow color and lower concentrations of green color. Most Argentine samples are distributed along the PC1 axis. However, one sample (A_Tar) is separated; this sample is different from the other Argentine samples but is not similar to those from Brazil and Paraguay. Paraguayan samples have higher concentrations of yellow color (positive part of PC2) and lower concentrations of green color. This way, Paraguayan and Brazilian samples are separated. The second component, with 30.60% of the variance, is responsible for the separation of Paraguayan samples, which are characterized by higher concentrations of yellow color (positive part of PC2) and lower concentrations of green color. Some yerba mate samples were grouped based on their color parameters. For instance, yerba mate samples from Argentina and from Paraguay are grouped closely together on the plot. These results were consistent with the findings of the AHC (Fig. 2).

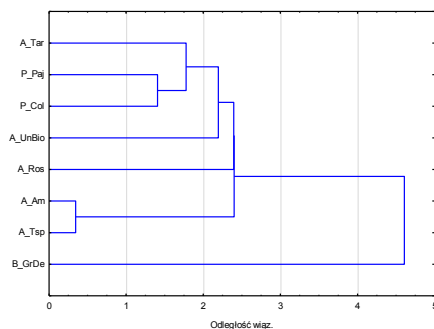


Fig. 2. The dendrogram drawn by agglomerative hierarchical clustering (AHC) of a total of 8 type of yerba mate

Rys. 2. Dendrogram (AHC) przedstawiający 8 typów yerba mate

Source: own study.

The dendrogram provides the visual data regarding the clustering of the 8 type of yerba mate samples, as well as the relationships between samples. Based on the dissimilarity of color parameters between yerba mate samples, the 8 yerba mate samples were divided into 3 clusters (cluster 1: A_Tar, P_Paj and P_Col; cluster 2: A_UnBio; cluster 3: A_AM and A_A_Tsp). It is interesting to note that yerba mate samples that originated from Argentina (A_Am, A_A_Tsp) were included in the same cluster, whereas the three yerba mate samples (P_Paj, P_Col and B_GrDe) that were from other country of origin were separated into two different clusters. These results imply that the color parameters are different in yerba mate origin from Argentina than in yerba mate from Paraguay and Brazil.

4. CONCLUSIONS

The interest of consumers in high quality foods with a clear geographical identity has grown rapidly. By nature, food products have a land-based, and therefore geographical origin. Historically, food consumption habits were shaped by socio-cultural factors and available local natural resources. Such links between food and territory have disappeared over time by various means. However, the last ten years consumers have a renewed interest in foods strongly identified with a place of origin [Dmowski and Kłopotek 2016]. The use of geographical indications (for instance, yerba mate from Paraguay or yerba mate from the special area of Argentina) allows producers to obtain market recognition and often a special (premium) price. False use of geographical indications by unauthorised parties is detrimental to consumers and legitimate producers. From this point of view, the development of new and increasingly sophisticated techniques for determining the geographical origin of

agricultural products is highly desirable for consumers, agricultural farmers, retailers and administrative authorities. It is an analytically challenging problem that is currently the focus of much attention within Europe and the USA.

This is the one of the first study providing an overall profile of the color parameters of *I. paraguariensis* to identify its region or country of origin.

The results point out that these models should be applied to distinguish yerba mate, but more analysis on yerba mate is necessary. However, the present models can be considered as not very stable but valid for the prediction of color parameters in distinguishing yerba mate, mainly for L*, a* and b* parameters. Also Marcelo et al. [12] in their study showed that the classification of yerba mate according to the country of origin in South America was possible by element concentration and chemometrics.

The classification of yerba mate according to the country of origin was possible by measure of color parameters in CIEL*a*b* system. The results presented here indicate that samples of yerba mate from Argentina (especially A_AM, A_Ros and A_Tsp) are very similar, almost the same, although they stated to be from different regions of origin. The same situation we can observe in samples from Paraguay and between samples from Argentina and Paraguay (A_Tar, A_UnBio and P_Paj, P_Col). It is noteworthy, that the sample of yerba mate from Brazil was characterized by different value of color parameters than other samples.

In summary, the CIEL*a*b* analysis, was able to differentiate the yerba mate samples based on their color parameters. From the results obtained we can conclude that the developed method can be useful for quality control of yerba mate and correct identification of its origin.

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