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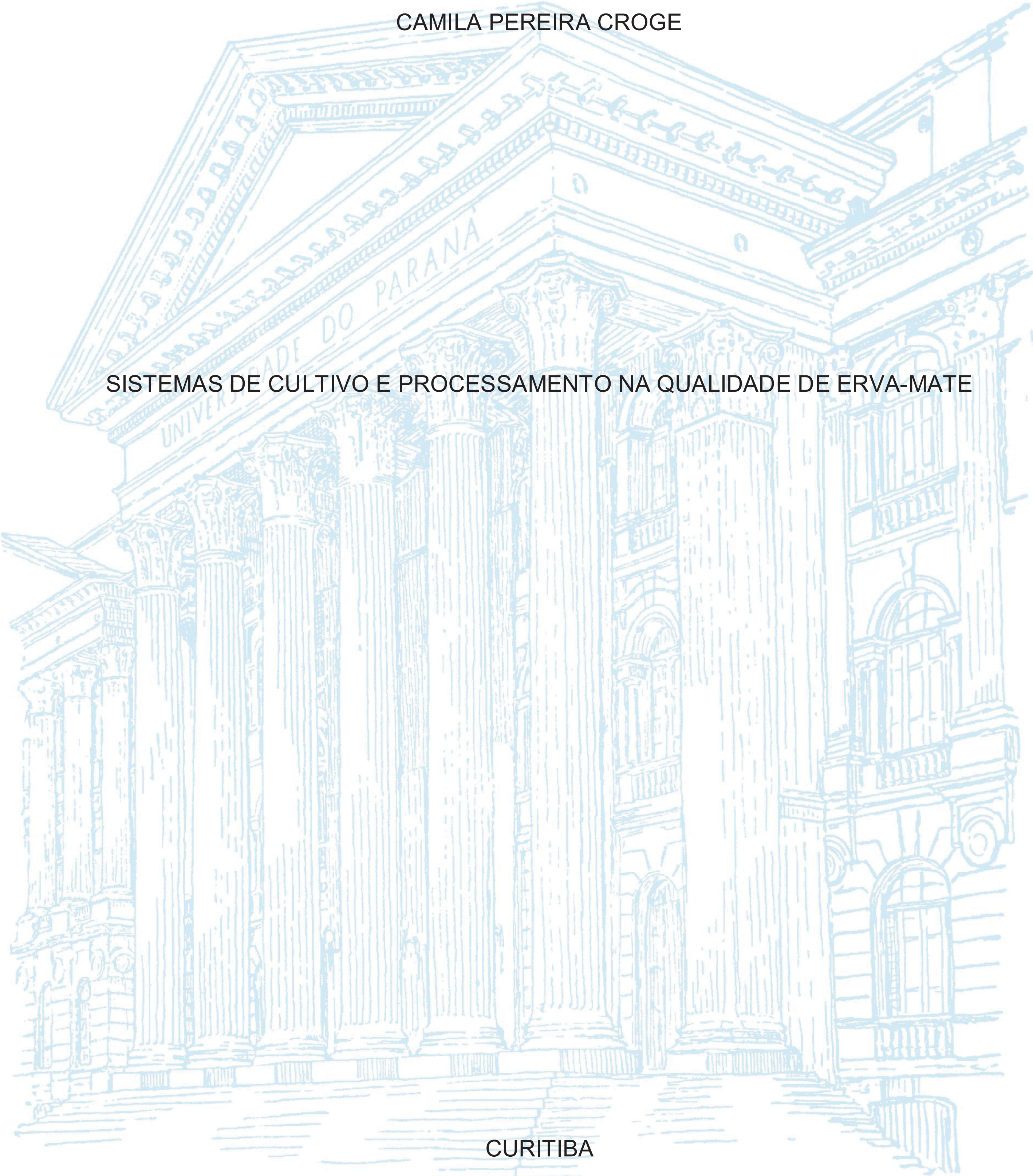

CAMILA PEREIRA CROGE

SISTEMAS DE CULTIVO E PROCESSAMENTO NA QUALIDADE DE ERVA-MATE

CURITIBA

2021

CAMILA PEREIRA CROGE

SISTEMAS DE CULTIVO E PROCESSAMENTO NA QUALIDADE DE ERVA-MATE

Tese apresentada ao curso de Pós-Graduação em Agronomia, Setor de Ciências Agrárias, Universidade Federal do Paraná, como requisito parcial à obtenção do título de Doutor em Ciências.

Orientadora: Profa. Dra. Francine Lorena Cuquel

Coorientadora: Profa. Dra. Paula Toshimi Matumoto Pintro

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TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em AGRONOMIA (PRODUÇÃO VEGETAL) da Universidade Federal do Paraná foram convocados para realizar a arguição da tese de Doutorado de **CAMILA PEREIRA CROGE** intitulada: **SISTEMAS DE CULTIVO E PROCESSAMENTO NA QUALIDADE DE ERVA-MATE**, sob orientação da Profa. Dra. FRANCINE LORENA CUQUEL, que após terem inquirido a aluna e realizada a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa.

A outorga do título de doutor está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

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Assinatura Eletrônica
26/02/2021 15:01:15.0
FRANCINE LORENA CUQUEL
Presidente da Banca Examinadora

Assinatura Eletrônica
14/04/2021 14:47:50.0
LAIS GOMES ADAMUCHIO DE OLIVEIRA
Avaliador Externo (INSTITUTO DE DESENVOLVIMENTO RURAL DO PARANÁ)

Assinatura Eletrônica
26/04/2021 15:34:37.0
MAYARA ALVES SCHRODER FONTANA
Avaliador Externo (CENTRO UNIVERSITÁRIO VALE DO IGUAÇU)

Assinatura Eletrônica
26/02/2021 17:13:52.0
LUIZ ANTONIO BIASI
Avaliador Interno (UNIVERSIDADE FEDERAL DO PARANÁ)

Assinatura Eletrônica
26/02/2021 15:15:14.0
PAULA TOSHIMI MATUMOTO-PINTRO
Avaliador Externo (UNIVERSIDADE ESTADUAL DE MARINGÁ)

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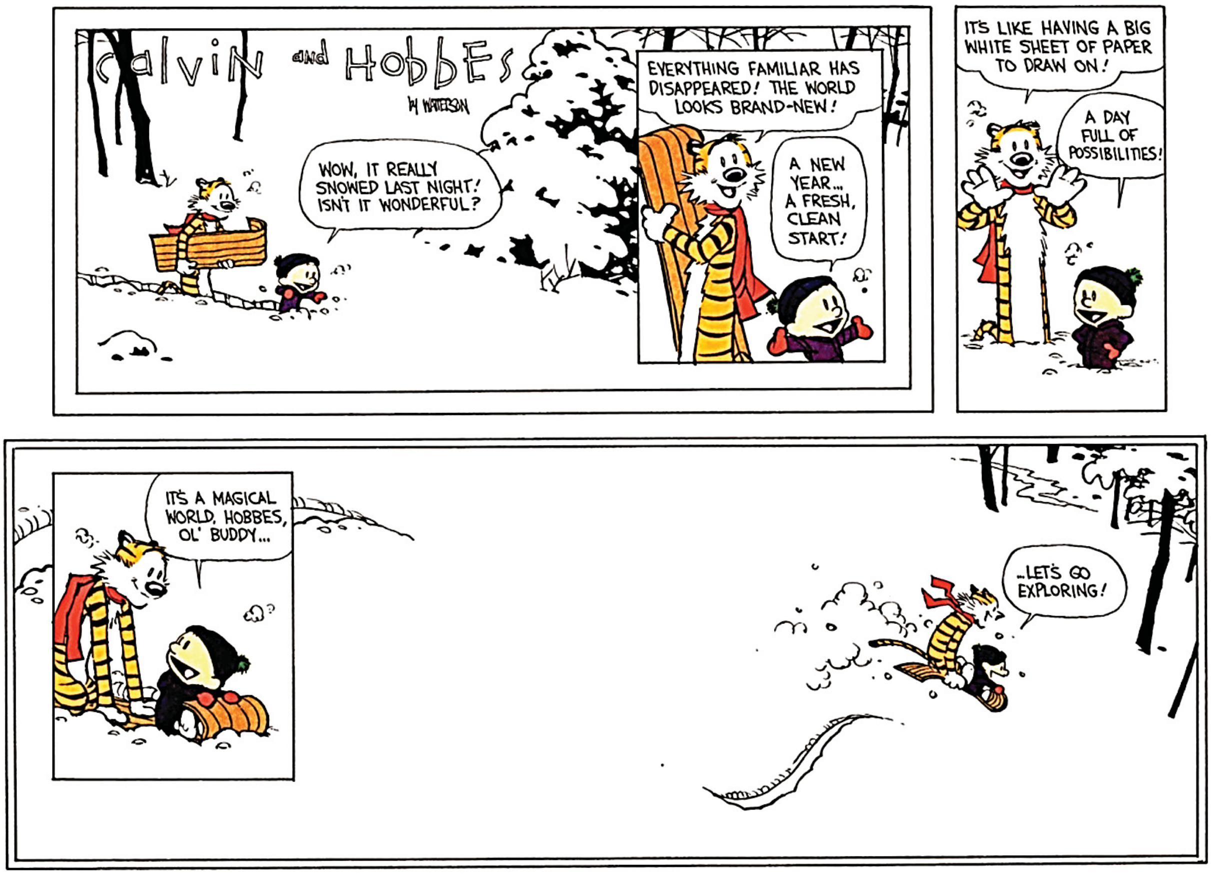
"*Não é sobre ter todas as pessoas do mundo pra si, é sobre saber que em algum lugar alguém zela por ti... É sobre ser abrigo e também ter morada em outros corações, e assim ter amigos contigo em todas as situações. A gente não pode ter tudo, qual seria a graça do mundo se fosse assim? Por isso, eu prefiro sorrisos e os presentes que a vida trouxe pra perto de mim*. "



(Bill Waterson, 1995, p. 371)

RESUMO

A erva-mate (*Ilex paraguariensis* A. St-Hil.) se configura como uma riqueza do sub-bosque de florestas de Araucárias na América do Sul. Se apresenta com uma composição química versátil que engloba compostos fenólicos e metilxantinas. Esses compostos são responsáveis por inúmeros benefícios à saúde que variam desde neuroproteção até a prevenção de doenças degenerativas. Porém, condições de cultivo, manejo e processamento podem alterar essa composição e estudos que elucidem essa relação são escassos. Nesse contexto, este trabalho visa subsidiar o manejo e o beneficiamento da erva-mate provenientes de diferentes sistemas de produção, bem como reconhecer qual a interferência das condições de cultivo e de processamento, em sua composição química e sensorial. Em última instância, pretende-se recomendar condições de manejo, cultivo e processamento ideais para a obtenção de matéria-prima de alta qualidade para ser utilizada em produtos energéticos e funcionais. Para isso, plantas oriundas de sistemas de produção em floresta nativa, floresta aberta e pleno sol foram avaliadas quanto a sua produção e composição físico-química. Além disso, foram realizadas quantificações de metilxantinas, compostos fenólicos e atividade antioxidante em relação as operações de processamento que a erva-mate é submetida. E, por fim, uma avaliação sensorial realizada com julgadores treinados foi elaborada buscando o perfil sensorial da erva-mate e sua correlação com sua composição química. Os resultados demonstraram que os diferentes sistemas de cultivo e suas características, bem como as épocas de colheita, alteraram a performance agronômica da erva-mate. O sistema de produção em floresta aberta se destacou por aliar qualidade e produtividade. As operações do processamento, por sua vez, proporcionaram mudanças na composição físico-quimica da erva-mate. Muitas perdas ocorrem no processo como um todo reduzindo os níveis dos compostos energéticos e antioxidantes. Além disso, ficou evidente que o sabor da erva-mate é diferenciado e que blends e moagens geram produtos com características sensoriais distintas.

Palavras-chave: *Ilex paraguariensis* A. St-Hil. Cultivo florestal. Avaliação sensorial. Compostos fenólicos. Metilxantinas.

ABSTRACT

Yerba Mate (*Ilex paraguariensis* A. St-Hil.) is considered a richness of the Araucaria forests understory in South America. It has versatile chemical composition that includes phenolic compounds and methylxanthines, which are responsible for numerous health benefits, which vary from neuroprotection to the prevention of degenerative diseases. However, cultivation, management and processing conditions can alter its composition and studies that elucidate this relationship are scarce. In this context, this work aims to subsidize the management and processing of yerba mate from different production systems and to evaluate the effect of cultivation and processing conditions on its chemical and sensory composition. This study also intended to recommend ideal management, cultivation and processing conditions for obtaining high-quality raw materials to be used in energy and functional products. For this, plants from native forest, open forest and full sun production systems were evaluated for their productivity, phenology and physicochemical composition. In addition, methylxanthines, phenolic compounds and antioxidant activity were quantified, considering the processing operations to which yerba mate is submitted. Finally, sensory evaluation was carried out with trained judges in order to quantify the sensory attributes of yerba mate and its correlation with its chemical composition. Results showed that the different cultivation systems and their characteristics changed the agronomic performance of yerba mate. The open forest production system stood out for combining quality and productivity. Processing operations, in turn, provided changes in the physicochemical composition of yerba mate. Many losses occur during processing as a whole, reducing the levels of energy and antioxidant compounds. Regarding the flavor of yerba mate, it was observed that different blends and milling processes generate products with different sensory characteristics.

Keywords: *Ilex paraguariensis* A. St-Hil. Forest cultivation. Sensory evaluation. Phenolic compounds. Methylxanthines.

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1 INTRODUCTION

Yerba mate (Ilex paraguariensis A. St-Hil.) is a richness of the Araucaria forests understory of South America. It has considerable economic value and significant importance in agricultural production systems, since in addition to income alternative, plays a strategic role in the preservation of native forest areas in ecosystems with perspective of multiple use of natural resources (VIBRANS et al., 2013; BARBOSA et al., 2020; CROGE et al., 2021).

Many South American regions had their initial growth driven by this activity and, even today, it still has economic, social and cultural relevance to the point of being considered the “green gold” in producing countries (Brazil, Argentina and Paraguay). Yerba mate produces different types of traditional energy drinks, such as “chimarrão” and green and toasted teas. In addition, other possibilities have been presented for the species, mainly as raw material for the nutraceutical, pharmaceutical and cosmetic industries (RIACHI et al., 2017; GULLÓN et al., 2018; MATEOS et al., 2018).

Its unique flavor and quality, recognized by consumers, are related to its chemical composition (GODOY et al., 2020). Rich in phenolic compounds, methylxanthines, chlorogenic acids, saponins, vitamins and minerals, yerba mate has many beneficial health effects ranging from neuroprotection to the prevention of highly prevalent degenerative diseases such as cancer (CITTADINI et al., 2019; TRIBBIA et al., 2019). In addition, it is used as a stimulant to improve energy and concentration in daily activities (CADONÁ et al., 2019). However, studies with this plant are still scarce, which started late compared to other species of similar economic and commercial potential such as Coffea sp. and Camelia sinensis (CROGE et al., 2021).

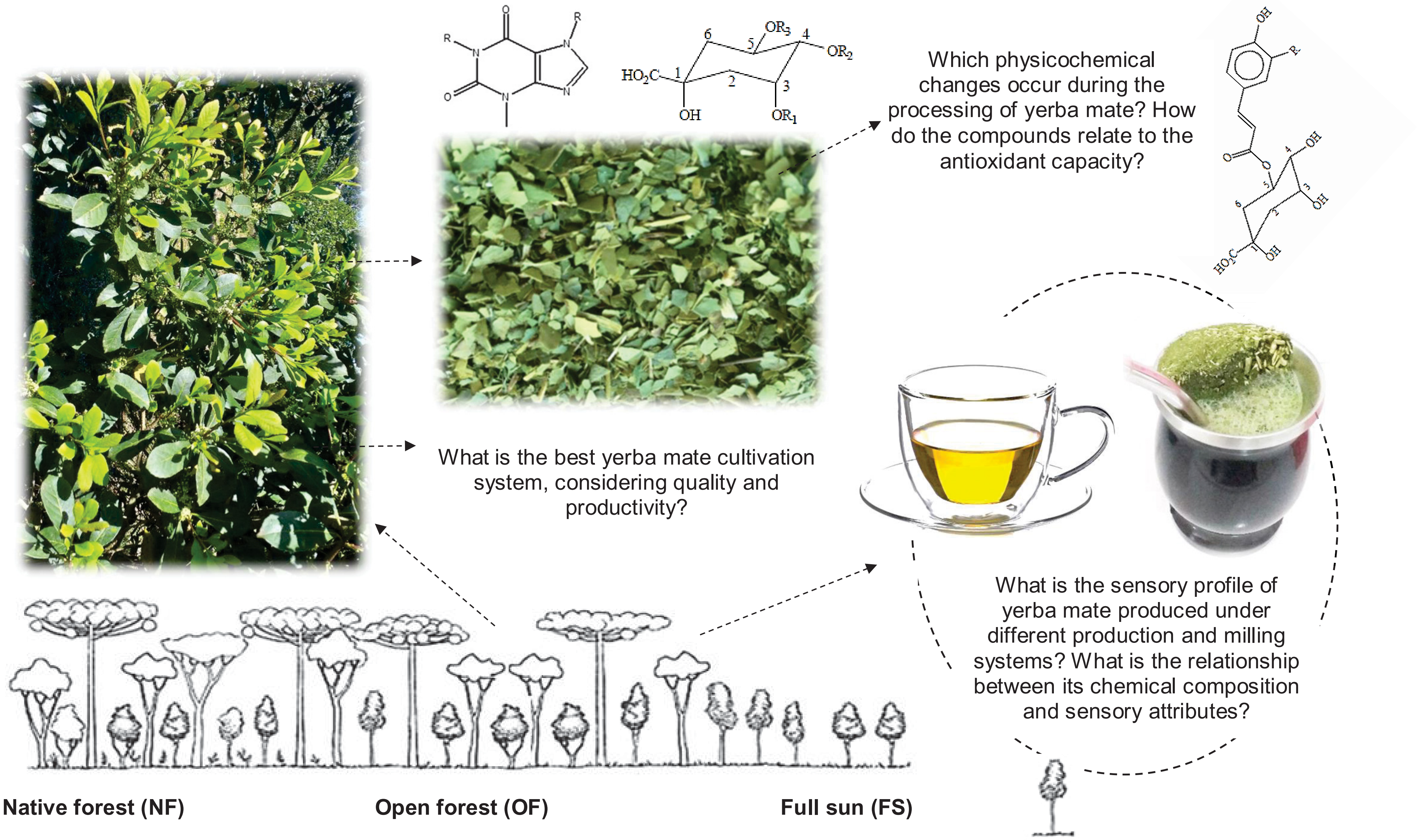
Due to its wide adaptation, yerba mate can be produced in shaded environments next to forests or even in systematic crops in full sun (DORTZBACH et al., 2018; BARBOSA et al., 2020; CROGE et al., 2021). However, its composition can vary considerably depending on cultivation and management conditions (BASTOS et al., 2018). In addition, after harvest, the different types of yerba mate processing can also contribute to change the contents of its chemical compounds and, consequently, its biological activity (DORTZBACH et al., 2018).

Regarding the factors that act in its composition, few studies have been carried out regarding quantitative determinations and the correlation with cultivation and processing conditions (CROGE et al., 2021). Little is known regarding the sensory quality of yerba mate. To date, few studies have been carried out aiming at defining the descriptors and the sensory profile of yerba mate products (GODOY et al., 2020).

Research on the chemical composition of yerba mate relating it to the different agronomic, industrial, sensory variables and consumer perception can be translated into an important tool for the implementation of the successful use and insertion of its products in the global market.

Thus, the aim of this study was to subsidize the management and processing of yerba mate from different production systems, as well as to identify the interference of cultivation and processing conditions on its chemical and sensory composition. Ultimately, it is intended to recommend ideal management, cultivation and processing conditions for obtaining high quality raw materials to be used in energy and functional products.

In this sense, an update of what has been researched about this species is initially presented, involving cultivation and processing systems, chemical composition and health benefits, followed by the search for understanding the interference of cultivation conditions in the production and biochemical composition of its leaves. The effect of unit operations on the quality of yerba mate in terms of phytochemical profile and antioxidant capacity was also evaluated. Finally, this study presents the sensory characteristics of yerba mate according to production variables and the way they are perceived by consumers (FIGURE 1).



What is the best yerba mate cultivation system, considering quality and productivity?

Which physicochemical changes occur during the processing of yerba mate? How do the compounds relate to the antioxidant capacity?

What is the sensory profile of yerba mate produced under different production and milling systems? What is the relationship between its chemical composition and sensory attributes?

FIGURA 1 – Graphic design of research developed with yerba mate in this study.

2 YERBA MATE: CULTIVATION SYSTEMS, PROCESSING AND CHEMICAL COMPOSITION. A REVIEW

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ABSTRACT: The unique chemical composition of yerba mate and its functionalities strongly suggest that its innovation potential needs to be explored. New uses would result in an increased consumption, exceeding the traditional consumption barrier and making yerba mate increasingly accessible on a global level. Thus, to highlight the importance of yerba mate as a potential source of agroeconomic resources, we present a review on its botanical, ecological, agronomic, and industrial aspects, along with information on the biochemical composition of this species and its biological activity.
Keywords: *Ilex paraguariensis* A. St-Hil., natural product, agroeconomic resources

2.1 INTRODUCTION

In recent years, the number of studies on yerba mate (*Ilex paraguariensis* A. St-Hil.) has increased, mainly focusing on its health effects. Yerba mate has several pharmacological activities, including antioxidant, anti-inflammatory, antimutagenic, anti-obesity, and cardioprotective functions (Gómez-Juaristi et al., 2018). These benefits are related to a unique chemical composition including alkaloids, polyphenols, terpenes, and essential oils, among others (Mateos et al., 2018; Riachi et al., 2018).

The species is abundant in the understory of Araucaria forests and has a considerable economic value and a significant importance in agricultural production systems, stabilizing incomes and playing a strategic role in the preservation of native forest areas in ecosystems with a multiple use perspective of natural resources (Inventário florístico floresta de Santa Catarina, 2013).

However, with some exceptions, the implementation of yerba mate, based on scientific evidence, had a late onset, while studies on *Camelia sinensis* and *Coffea* sp.

are numerous. Compared to mate, these species have a similar economic and biological potential and are widely consumed worldwide due to their stimulating effects on the nervous system (Heck and Mejia, 2007; Baeza et al., 2017). The consumption of infusions prepared from the leaves of yerba mate can be traced back to the XIX century, while studies with this species have only be performed in the last three decades (Heck and Mejia, 2007).

Our current knowledge about yerba mate is rather fragmented, calling for further studies. The species has potential to not only be used as a drink, but also as raw material for the cosmetics, nutraceutical, and pharmaceutical industries (Heck and Mejia, 2007; Bracesco et al., 2011; Berté et al., 2014; Souza et al., 2015; Cardoso Junior and Morand, 2016). This, however, would involve changes in the agronomic research to obtain a high-quality raw material through breeding programs, variety selection, and production strategies in efficient systems that ensure the best chemical composition, thereby optimizing its biological activities (Cardoso Junior and Morand, 2016).

Thus, to emphasize the importance of this species as potential source of agroeconomic resources and highlight its versatile chemical composition and the possibility of multiple uses, a literature review on its botanical, ecological, agronomic, and industrial aspects is presented. In addition, information on its biochemical composition and biological activity is also included.

2.2 CLASSIFICATION AND BOTANICAL ASPECTS

Yerba mate has first been described in 1822 by the French naturalist Auguste de Saint-Hilaire, who published in “Mémoires du Muséum d'Histoire Naturelle” in France. His observations described a perennial tree with many branches and leaves, a relatively developed size, and an outline that resembled that of cypresses. The leaves are dark green in the ventral aspect and odorless when fresh, but with a herbaceous and bitter flavor. When prepared for consumption, the faint odor is reminiscent of the aroma of Swiss tea (Berté et al., 2014). Their complete botanical classification is shown in Figure 1.

Yerba mate is a perennial tree of the family Aquifoliaceae, which can reach a height of 8 to 15 m. Its leaves are perennial, alternating, coriaceous, obovate to elliptic, with slightly shallow margins, an obtuse apex, and a wedge-shaped base. The petioles are up to 15 mm in length. In its original habitat, flowering occurs from Oct to Dec; the inflorescences are pistils in fascicles, with monoic flowers that can appear grouped in the axilla, petals and rounded ones. The fruits are drupes ranging from red to black, oval to globose, with a diameter of 4.5-6.5 mm diameter and four to five seeds (Figure 2) (Bracesco et al., 2011; Cabral et al., 2018).

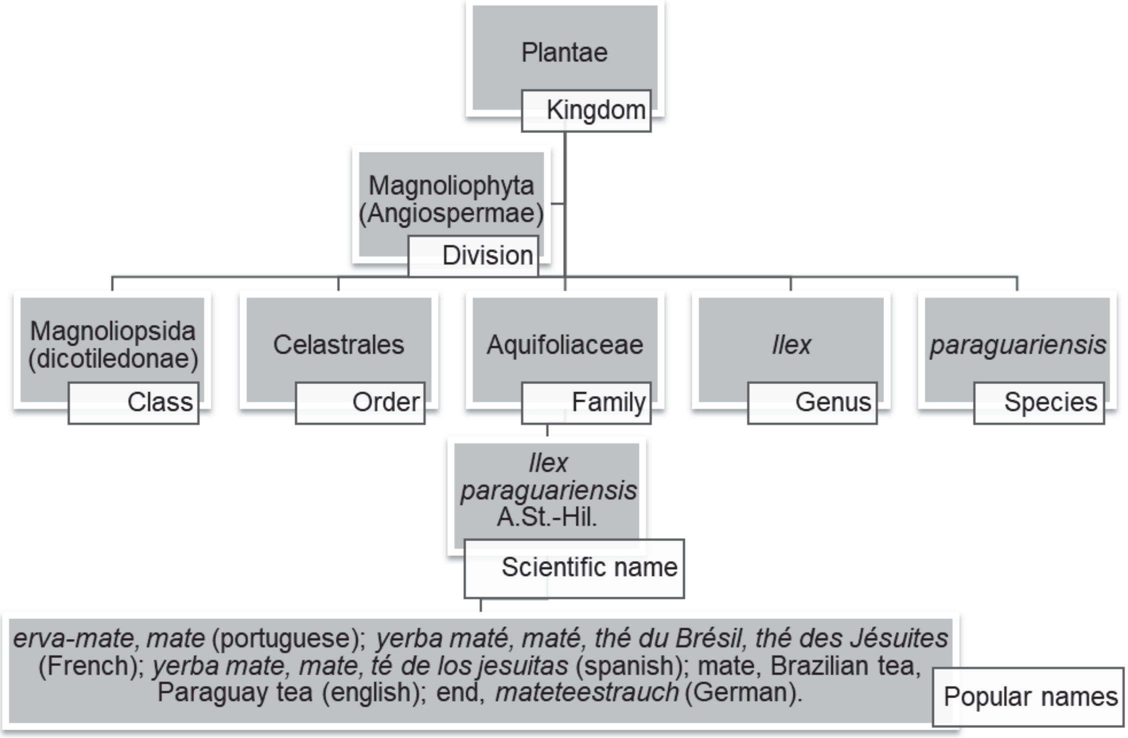

Figure 1 – Botanical classification of yerba mate (Bracesco et al., 2011; Cabral et al., 2018).

2.3 ECOLOGICAL ASPECTS AND GEOGRAPHICAL DISTRIBUTION

The Family Aquifoliaceae, in its present constituency, is represented solely by the genus Ilex, with more than 600 species. Ilex has a predominantly tropical distribution, extending to temperate regions of the Northern and Southern hemispheres, with East Asia and South America as the global centers of diversity (Yi et al., 2017; Cabral et al., 2018).

Yerba mate is the most commercially important species of the genus and occurs in its native state in the subtropical and temperate regions of South America, including

Argentina, Brazil, and Paraguay, between latitudes 21°00’00’ S and 30°00’00’’ S and longitudes 48°30’00’’W and 56°10’00’’W (Figure 3), preferably at altitudes between 500 and 1,500 m (Heck and Mejia, 2007; Chaimsohn et al., 2014). About 80 % the species are native to Brazil and mainly distributed in the states of Parana, Santa Catarina, and Rio Grande do Sul (CEPA, 2015).

Figure 2 – Yerba mate: tree, leaves, branches and flowers – A) tree; B) flowering; C) leaves and branches. (Source: A and C = Author; B = Herbário Dr. Roberto Miguel Klein (FURB), 2018).

The species are endemic and distributed in the wild exclusively in the forested regions of South America, composed of Mixed Ombrophilous Forest, in the Atlantic

Forest biome, always in associations, and clearly evolved with Araucaria angustifolia (Heck and Mejia, 2007). To develop, Ilex requires average annual temperatures between 17 and 21 °C and regular rainfall, with a high air and soil humidity. It occurs in the sub-forest layer in acidic soils of low natural fertility, a high aluminum content, low available phosphorus levels, and a high organic matter concentration; it tolerates shade at any age and considered an ombrophilous species with slow or moderate growth, typical of mature forests, where it can reach density of hundreds individuals per hectare (Caron et al., 2014b; Chaimsohn et al., 2014).

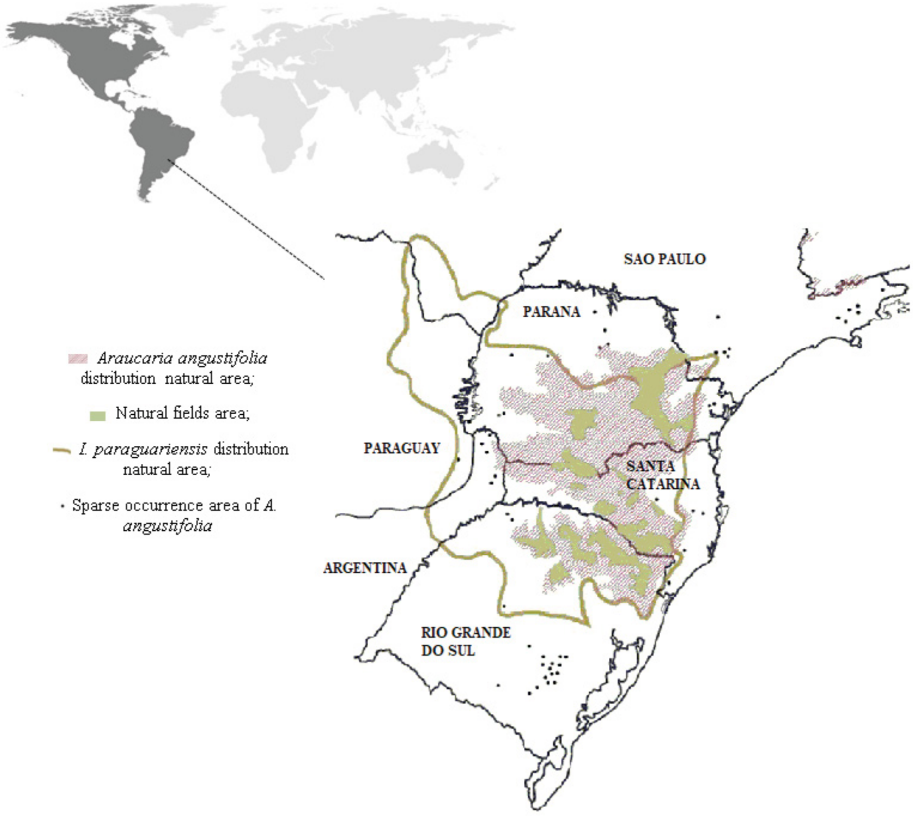

Figure 3 – Natural distribution area of yerba mate. Adapted from Voigt et al., 2016.

2.4 AGRONOMIC ASPECTS - CROPPING SYSTEMS

The world production of yerba mate in 2016 was 937,310 tons, mainly coming from Brazil, Argentina, and Paraguay (FAO, 2017). In Araucaria forests, the species is abundant and has a considerable economic value and a significant importance in agricultural production systems, becoming a stabilizing factor of the income and having, many times, a strategic function of preservation of areas of native forests in their ecosystems with perspective of multiple use of the natural resources (Marques et al., 2014; Pires et al., 2016).

In general, herbs occur is diverse habitats, based on their adaptability to different light conditions and management strategies, enabling different designs of production systems. In this sense, we highlight the extractive systems, consorted with native forests, agroforestry, and monoculture (full sun) (Marques et al., 2014; Vogt et al., 2016).

The extractive exploitation of a natural forest (Araucaria Forest or Ombrófila Mista) is considered as the traditional system of cultivation, mainly in terms of native herbs. Yerba mate produced in such a system is extracted sustainably from the most significant native forest areas of southern Brazil. In this system, management or cultural treatments are not common, and the crops are harvested periodically (Marques et al., 2014; Vogt et al., 2016).

A system in consortium with native forest, also called “mixed cultivation” or “caívas”, is traditionally the exploitation of forest remnants where yerba mate grows naturally or in cultivation, managed in association with other plant species, usually native species, and, in some cases, even associated with animal husbandry. This system also has economic, social, and environmental importance, since it contributes to the preservation of forest remnants and generates income to the farmer (Chaimsohn et al., 2014).

Most of these caívas are forest fragments of varying sizes in rural properties of southern Parana and northern Santa Catarina (Figure 4). The set of these fragments in the region contributes to the formation of the landscape, composing a mosaic of cultivated areas interspersed by forests (Hanisch et al., 2010).

The agroforestry system is the cultivation of yerba mate associated with logging and/or agricultural exploitation. These systems are composed of plant species in the arboreal and/or herbaceous-shrub layer and managed in a way that favors the production of yerba mate in the understory. The species planted have different cycles, sizes, and functions, resulting in an increased biodiversity, which promotes physical-chemical, hydrological, and microbiological improvements of the soil, besides generating income (Barbosa et al., 2017).

Monocultures allow the cultivation of more plants in a given area, higher yields, and mechanized harvesting. However, the trees are exposed to full sun, which can lead to alterations in their metabolic processes and to damages in the leaf quality. These species have evolved as ombrophilous species, and, when cultivated in open places, are subjected to physiological stresses, making them more susceptible to pest attacks and diseases (Marques et al., 2014).

Figure 4 - Forest fragment with Yerba mate (north of Santa Catarina – Três Barras, Campininha, 2020).

The maintenance of native herbs in traditional systems (extractive and intercropped with native forests) can represent an important stimulus for environmental conservation due to the need to maintain the forest and its significant economic value, providing monetary value for forest remnants. In addition, such systems generally have fewer phytosanitary problems, favoring plant production without the use of agrochemicals (Marques et al., 2012; Chaimsohn et al., 2014). The characteristics of both are common, such as shading of plants, the presence of other forest species and sometimes the conservation of the original material of mate (Marques et al., 2014).

In addition to the significant volume of yerba mate produced in traditional and agroforestry systems, the product obtained from such systems is more highly valued than that obtained from cultivated plants, since the shading by other tree species results in a product with a better flavor which is better accepted in the national and Uruguayan market (the largest consumer in the world) (Marques et al., 2012). The industrial demands for this type of weed have increased markedly in recent years (Caron et al., 2014a; Caron et al., 2014b).

The composition of the yerba mate varies considerably depending on factors such as seasonality, temperature, water and nutrient availability, cultivation system, and adopted management practice, with effects on its physiological effects. Thus, studies that elucidate the relationship between its composition and its constituent factors are necessary to determine the association between health, mate consumption, and the maintenance of sustainable supply chains with forest preservation (Berté et al., 2014; Pires et al., 2016; Cardoso Junior and Morand, 2016; Kahmann et al., 2017; Riachi et al., 2018).

2.5 PROCESSING AND USES

The first explorers of yerba mate were the native inhabitants of the Northeast of Argentina, the South of Brazil, Paraguay, and Uruguay, who used it because of its stimulating and medicinal properties. By several tribes, such as the Guaranis, the Amerindians (Incas and Quechuas), and the Caingangues, its leaves were consumed, infused, or chewed. Infusion of the leaves became a popular drink, and to this day, the product obtained from dry leaves, also called mate or maté, is used for the preparation of several types of infusions, such as the chimarrão, tereré, and mate tea (roasted leaves) (Holowatt et al., 2016; Lima et al., 2016).

Yerba mate exploration is based on the use of selected leaves and branches, which are subjected to thermal bleaching (sapeco) for enzyme inactivation, followed by drying, grinding, and separation. These last two steps allow obtaining a product with standard granulometry, followed by milling and, depending on the desired product, aging for up to 24 months (Figure 5). The intensity, the grinding type, and the aging period result in products with differentiated standards (Meinhart et al., 2010).

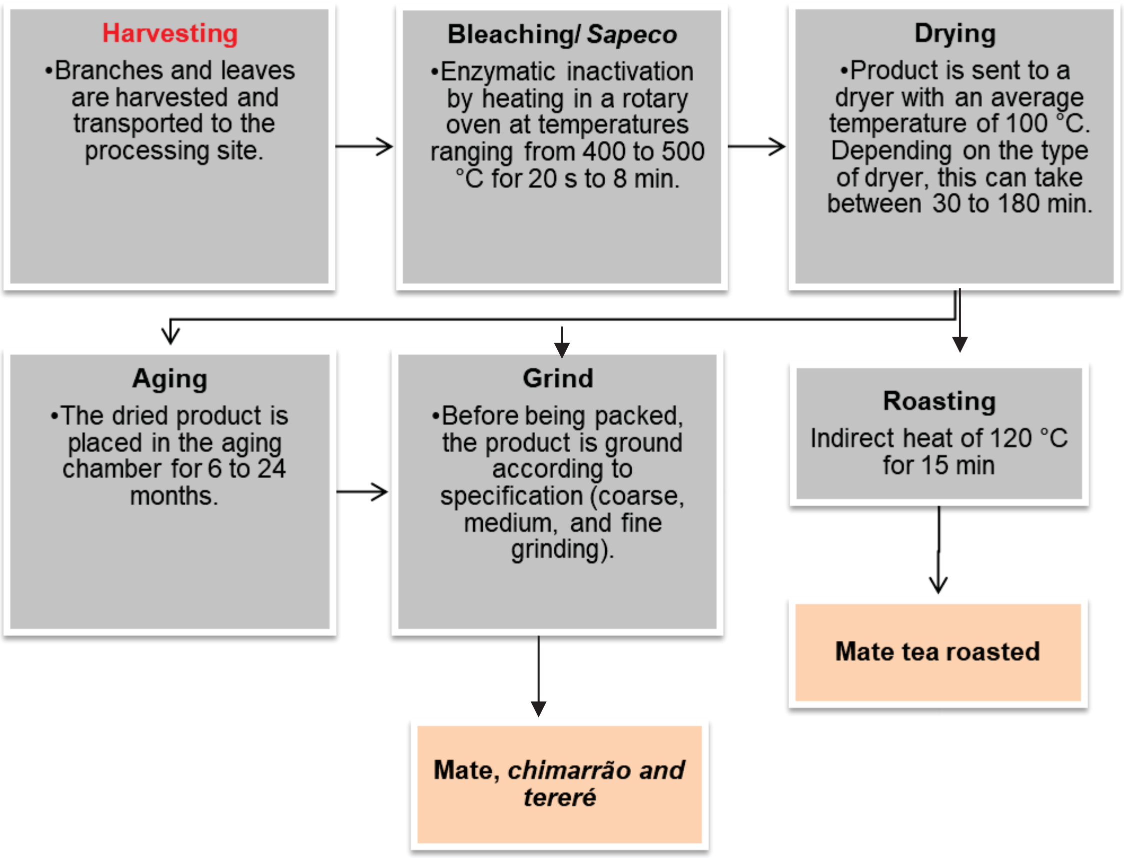

Figure 5 – Traditional processing of yerba mate (Berté et al., 2014; Silveira et al., 2017; Riachi et al., 2018).

The agro-industrial processing of yerba mate has not significantly been altered since the beginning of its economic exploitation, with disadvantages related to its high energy requirement, difficulties in controlling its variables and, consequently, in the standardization of the final product. Another negative aspect concerns the oxidative environment of the bleaching and drying process, potentially contributing to the degradation of the biochemical compounds of the leaves. Thus, the development of new technological processes for the preservation of its compounds is a strategy that must be considered (Meinhart et al., 2010; Cardoso Junior and Morand, 2016).

Mate is consumed as a leaf infusion, with variations in the manufacturing and preparation of the beverage. The leaves are infused with hot water and gradually ingested by means of a pump and gourd; tereré is a cold drink, while mate tea is obtained from the roasted leaves and consumed hot or cold (Bracesco et al., 2011; Cardoso Junior and Morand, 2016).

Roasted mate can also be subjected to the extraction of soluble solids with hot water, followed by drying in a spray-dryer, resulting in soluble roasted mate. Soluble solid extraction from the crushed green yerba mate yields the soluble green mate; both products are primarily intended for export and present as market innovation (Berté et al., 2014).

The per capita consumption of yerba mate in Uruguay, Argentina, and Brazil is estimated at 8 to 10 kg yr^{-1}, 5 to 6 kg yr^{-1}, and 1.2 to 5 kg yr^{-1}, respectively (Berté et al., 2014; Cardoso Junior and Morand, 2016). In Brazil, the state of Rio Grande do Sul is the largest consumer of herb for chimarrão (70,000 t yr^{-1}), while Rio de Janeiro is the largest consumer of roasted mate tea (1,500 t yr^{-1}). In Brazil, the entire yield is exported, mainly to Uruguay and Chile, followed by the USA, Europe, and Asia, which receive the product as whole or ground dried leaves or in the form of extracts for the pharmaceutical industry (Anesine et al., 2012; Lima et al., 2016).

In the last decade, along with traditional use, yerba mate has been grown for raw material in the production of beers, soft drinks, cosmetics, sweets, and functional cheeses as well as other non-traditional uses (Table 1). In the case of functional cheeses, a recent study shows that the addition of yerba mate, besides increasing the biological activities due to the interaction between herb polyphenols and milk proteins, increases the sensorial characteristics, with good acceptance by consumers (Marcelo et al., 2014; Saraiva et al., 2019).

The leaves are also used to produce energy drinks as an alternative to coffee, which are widely appreciated in Europe and the United States because of their high levels of antioxidants and their nutritional benefits (Bercher et al., 2011; Bergottini et al., 2017). However, studies aiming to implement new uses, such as food preservatives, food supplements, dyes, or hygiene and cosmetics products, need to be implemented in a way that consumption exceeds the traditional consumption barrier and becomes increasingly accessible in Latin America, which is also interesting for innovations in the agri-food sector (Table 1) (Cardoso Junior and Morand, 2016).

As a secondary use, the wood of yerba mate produces a blade of excellent quality (Table 1). However, for the generation of energy, pulp, and paper, the species is considered inadequate. Its residue, after processing, has been used by horticultural workers as organic fertilizer and in animal feed, providing forage with 13 % crude protein. In addition, the species is highly recommended because of its ornamental value and biological properties, mainly for afforestation, gardening, and the ecological restoration of degraded ecosystems (Embrapa, 2019).

Table 1 – Yerba mate uses

Plant components	Application	Uses
Leaves and branches	Traditional uses (beverages)	Chimarrão, tereré, mate tea (roasted leaves), blend of yerba mate with herbs and flavored tea.
	Non-traditional uses (beverages)	Freeze dried extract, tea (green leaves), tea capsule (roasted and green leaves), mate latte, energy drinks, beers, soft drinks, liqueur.
	Functional foods	Sweets, jam, breaded, functional cheeses.
	Cosmetics	Shampoo, soap, anti-aging cream, moisturizing cream.
	Natural antioxidant (additive)	Aqueous dipping solution to minimizing browning development of freshly fruits; Biodegradable edible films to be used as packaging for fruits.
	Textile industry	Dyeing silk, wool, linen and cotton fabrics.
Fruits	Cosmetics	Oil essential; Anti-aging cream, moisturizing cream.
	Vegetable extracts of the unripe fruits	Molluscicides
Seeds	Ornamental value and biological properties (seedlings)	Afforestation; Gardening; The ecological restoration of degraded ecosystems.
Wood	Wood industry	Blade of excellent quality
Residue (after processing)	Agriculture	Organic fertilizer.
	Livestock	Animal feed.

Rodríguez-Arzuaga and Piagentini (2017) optimized the yerba mate concentrations in an aqueous dipping solution with the aim of maximizing the antioxidant capacity and minimizing browning development without affecting the sensory quality of freshly cut apples. Our results suggest that chemical treatment with yerba mate applied to freshly cut apples was successful in delaying enzymatic browning development, providing compounds with antioxidant capacity with potential benefit for human health (Table 1).

Biodegradable and edible starch-glycerol based films containing different concentrations of a natural antioxidant as yerba mate extract were evaluated with the aim to obtain promising biodegradable edible films to be used as packaging. The study demonstrated that yerba mate extract acted as a plasticizer when it was incorporated as an antioxidant into starch-glycerol based films. Besides, the use of the extract improved the biodegradability of the films in compost and preserved their stability (Medina Jaramillo et al., 2016).

Yerba mate was used for dyeing silk, wool, linen and cotton fabrics; dyed silk fabrics present the highest color strength (Yoo and Jeon, 2012). Giacomini et al. (2016) investigated the best dyeing conditions, such as pH, temperature and dyestuff concentration of silk fabric using roasted yerba mate. The authors concluded that silk fabrics can be easily dyed with yerba mate, providing yellowish brown color, and the best silk dyeing result was achieved using temperature 90 °C, pH 3.0 and 20 g L–1 dye concentration. Bulut and Akar (2012) used some oil-free yerba mate wastes to dye cotton and wool yarn previously cationized without metal salts. Fabrics were successfully dyed with high color strength.

Another study aimed to evaluate the effectiveness of extracts of the unripe fruits of yerba mate for the chemical control of piped apple snail (Pomacea canaliculata) and non-target species such as South American catfish (Rhamdia quelen) under laboratory conditions. The extracts were particularly attractive considering the source of the compounds and their effectiveness as molluscicides (Brito et al., 2018).

2.6 CHEMICAL ASPECTS, BIOACTIVE COMPOUNDS AND THEIR FUNCTIONALITIES

Much attention has been dedicated to yerba mate due to the potential health benefits associated with its consumption (Figure 5). These benefits seem to be related to their phytochemical variability, determining the unique chemical composition. Studies have detected different chemical groups such as polyphenols, saponins, alkaloids, and essential oils (Tables 2, 3 and 4). The leaves also contain vitamins (A, C, B1, and B2), magnesium, calcium, iron, zinc, sodium, and potassium (Heck and Mejia, 2007; Berte et al., 2014).

Table 2 - Phenolic compounds found in yerba mate (2015-2018).

Chemical composition	Sample	Content	Unity	References
Total phenolic compounds	Leaves, green branches, extracts	9.45 to 8047.00	mg 100 g^{-1}	Souza et al., 2015; Mateos et al., 2018; Holowaty et al., 2016
	Infusions of *tereré* or *chimarrão*	143. 98 to 1194.90	mg 100 mL^{-1}	Gebara et al., 2017; Baeza et al., 2017
	Fruits	59.25 to 62.25	mg 100 g^{-1}	Fernandes et al., 2016;
	Instant mate	343.17	µmol 100 g^{-1}	Oliveira et al., 2017
Total flavonoids	Leaves, green branches, extracts	3.06 to 757.00	mg 100 g^{-1}	Souza et al., 2015; Mateos et al., 2018
Anthocyanins	Fruits	17.52 to 43.79	mg 100 g^{-1}	Fernandes et al., 2016
Rutin	Leaves, green branches, extracts	1.86 to 6.10	mg g^{-1}	Silveira et al., 2017; Baeza et al., 2017; Mateos et al., 2018
	Infusions of *tereré* or *chimarrão*	1.93	mg 100 mL^{-1}	Silveira et al., 2017
	Fruits	10.96 to 11.72	mg 100 g^{-1}	Fernandes et al., 2016
	Instant mate	3.60	µmol 100 g^{-1}	Oliveira et al., 2017

Table 3 – Phenolic acid content found in yerba mate (2015 – 2018).

Chemical composition	Sample	Content	Unity	References
Caffeic acid	Leaves, green branches, extracts	4.92 to 12.20	mg 100 g^{-1}	Souza et al., 2015
	Infusions of *tereré* or *chimarrão*	0.04 to 0.10	mg 100 mL^{-1}	Silveira et al., 2017; Riachi et al., 2018
	Leaves	11.47	mg 100 g^{-1}	Souza et al., 2015; Lima et al., 2016;
	Fruits	15.72 to 21.49	mg 100 g^{-1}	Fernandes et al., 2016
	Roasted mate	3.90	mg 100 g^{-1}	Lima et al., 2016
3 – CQA	Leaves, green branches, extracts	14.00	mg 100 mL^{-1}	Meinhart et al., 2018
	Infusions of *tereré* or *chimarrão*	3801.90 to 27628.33	mg 100 g^{-1}	Lima et al., 2016; Meinhart et al., 2017
	Roasted mate	539.10	mg 100 g^{-1}	Lima et al., 2016
	Instant mate	65.28	µmol 100 g^{-1}	Oliveira et al., 2017

Table 3 (continuation) – Phenolic acid content found in yerba mate (2015 – 2018).

Chemical composition	Sample	Content	Unity	References
4 – CQA	Leaves, green branches, extracts	1179.50 to 6805.91	mg 100 g^{-1}	Lima et al., 2016; Meinhart et al., 2017
	Infusions of *tereré* or *chimarrão*	5090.00	µg 100 mL^{-1}	Meinhart et al., 2018
	Roasted mate	788.50	mg 100 g^{-1}	Lima et al., 2016
	Instant mate	68.68	µmol 100 g^{-1}	Oliveira et al., 2017
5 – CQA or chlorogenic acid	Leaves, green branches, extracts	43.10 to 1207.04	mg 100 g^{-1}	Lima et al., 2016; Meinhart et al., 2017; Souza et al., 2015; Mateos et al., 2018
	Infusions of *tereré* or *chimarrão*	3.66 to 50.00	mg 100mL^{-1}	Meinhart et al., 2018; Silveira et al., 2017; Butiuk et al., 2016; Riachi et al., 2018
	Fruits	13.58 to 15.85	mg 100 g^{-1}	Fernandes et al., 2016
	Roasted mate	929.50	mg 100 g^{-1}	Lima et al., 2016
	Instant mate	80.42	µmol.100 g^{-1}	Oliveira et al., 2017
3,4-Dicaffeoylquinic acid	Leaves, green branches, extracts	10.30 to 582.00	mg 100 g^{-1}	Souza et al., 2015; Lima et al., 2016; Baeza et al., 2017; Meinhart et al., 2017
	Infusions of *tereré* or *chimarrão*	0.70 to 6.43	mg 100 mL^{-1}	Silveira et al., 2017; Meinhart et al., 2018
	Roasted mate	0.41	mg 100 mL^{-1}	Silveira et al., 2017
	Roasted mate	101.60	mg 100 g^{-1}	Lima et al., 2016
3,5-Dicaffeoylquinic acid	Leaves, green branches, extracts	29.51 to 7265.00	mg 100 g^{-1}	Souza et al., 2015; Lima et al., 2016; Baeza et al., 2017; Meinhart et al., 2017.
	Infusions of *tereré* or *chimarrão*	7.60 to 29.51	mg 100 mL^{-1}	Silveira et al., 2017; Meinhart et al., 2018
	Roasted mate	0.45	mg 100 mL^{-1}	Silveira et al., 2017;
	Roasted mate	191.50	mg 100 g^{-1}	Lima et al., 2016
4,5-Dicaffeoylquinic acid	Leaves, green branches, extracts	21.20 to 3913.00	mg 100 g^{-1}	Souza et al., 2015; Lima et al., 2016; Baeza et al., 2017; Meinhart et al., 2017.
	Infusions of *tereré* or *chimarrão*	1.80 to 7.49	mg 100 mL^{-1}	Silveira et al., 2017; Meinhart et al., 2018;
	Roasted mate	0.86	mg 100 mL^{-1}	Silveira et al., 2017
	Roasted mate	346.90	mg 100 g^{-1}	Lima et al., 2016

Table 4 – Methylxanthine contents found in yerba mate (2015 – 2018).

Chemical composition	Sample	Content	Unity	References
Caffeine	Leaves, green branches, extracts	7.10 to 32.23	mg g^{-1}	Holowaty et al., 2016; Friedrich et al., 2017; Konieczynski et al., 2017
	Infusions of *tereré* or *chimarrão*	6.30 to 68.30	mg 100 mL^{-1}	Gebara et al., 2017
	Fruits	8.04 to 8.11	mg 100 g^{-1}	Fernandes et al., 2016
Theobromine	Leaves, green branches, extracts	1.12 to 4.38	mg g^{-1}	Friedrich et al., 2017; Konieczynski et al., 2017; Mateos et al., 2018
	Fruits	2.56 to 4.06	mg 100 g^{-1}	Fernandes et al., 2016
Theophylline	Infusions of *tereré* or *chimarrão*	1.58	mg g^{-1}	Konieczynski et al., 2017

Compounds such as polyphenols, saponins, alkaloids, and essential oils originate from the secondary metabolism of plants and, because of their chemical diversity, exhibit a variety of functions in plants. Numerous substances act as defense compounds against herbivores and pathogens, while others play a role in mechanical support, pollinator or fruit disperser attraction, protection against ultraviolet radiation, or the reduction of the growth of adjacent competing plants (Taiz et al., 2017; Neugart et al., 2018).

Yerba mate samples obtained at different processing steps were analyzed for chlorogenic acids content. The highest content was found in green leaves and stems (Butiuk et al., 2016). Structurally, chlorogenic acids are a family of non-flavonoid phenolic compounds, comprising caffeic and quinic acid esters and their mono and dicaffeoylquinic isomers. Chlorogenic acid (5-CQA) isomers include 3-O-caffeoyl-quinicacid (3-CQA), 4-O-caffeoyl-quinic (4-CQA), 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid and 4,5-dicaffeoylquinic acid (Table 3). Potentially beneficial properties to humans such as antioxidant, hypoglycaemic, antiviral and hepatoprotective activities have been also attributed to chlorogenic acids in in vitro, in vivo and epidemiological studies (Butiuk et al., 2016; Meinhart et al., 2018; Riachi et al., 2018).

In addition, caffeine, theophylline and theobromine alkaloids are important active components of yerba mate, which are derived from xanthine and also known as methylxanthines (Table 4). They all have in common the stimulating effect on the central nervous system, with caffeine as the most potent representative. Methylxanthines also affect the cardiovascular system, with theophylline generating the strongest effect. Thus, caffeine, theophylline, and theobromine concentrations in yerba mate beverages is generally of great interest (Holowaty et al., 2016; Friedrich et al., 2017; Konieczynski et al., 2017).

The biochemical composition of yerba mate varies according to the locality and mode of cultivation or to the processing method. The contents of yerba mate can vary widely (Table 2), and the environmental conditions to which the plants are submitted (factors such as seasonality, temperature, water and nutrient availability, radiation) determine their biosynthesis (Dutra et al., 2010; Pires et al., 2016).

Thus, the cultivation and management systems highly impact the levels of these substances (Dutra et al., 2010; Berté et al., 2014). Thereby affecting the final quality of the product and its effect on human health. However, studies that interrelate these factors are still scarce (Heck and Mejia, 2007; Neugart et al., 2018; Riachi et al., 2018).

2.7 FINAL REMARKS

Statistics of consumption show that the production chain of yerba mate is based on the use of traditional drinks such as the chimarrão and the tereré. However, considering its chemical composition and functionalities, it is evident that its innovation potential still needs to be explored. The implementation of new uses, such as food preservatives, food supplements, dyes, hygiene and cosmetic products, is necessary to increase yerba mate consumption worldwide. In addition, studies that explain the interference of crop systems in chemical composition and product quality need to be developed.

Anti-obesity potential; Promotes body weight, body mass index and waist circumference reduction (Luís et al., 2019).

Maintenance of basal locomotor activity, normalized anxiety-like activity; effective prevention of morphological damage due to to chronic stress (Lima et al., 2018).

Adjuvant in Parkinson tratament with impact on the quality of life (Tribbia et al., 2019).

Protects HDL cholesterol and glucose, also avoiding hepatic steatosis (Valenca et al., 2019).

Promotes an effect on osteoblast differentiation (a concentration-specific direct stimulatory effect) (Balera-Brito et al., 2019).

Reduces the risk of age-associated neuropathologies; increases resistance against oxidative stress; delays Aβ-induced paralysis (Machado et al., 2019)

Prevention of retinal damage in age-related macular and other retinal degenerations where oxidative stress is a pathogenic mechanism (Tate et al., 2020).

Inhibition of intermittent ROS generation promoted by exercise, which reduced adaptive response in heart; cardioprotection induction (Cahuê et al., 2019).

Neuroprotective effects; attenuating lung cancer-related neuroinflammation and damage; prevention of lung adenocarcinoma deleterious effects on murine brain (Cittadini et al., 2019a; Cittadini et al., 2019b).

Favourably affects leukocytes' p47phox expression, inflammatory cytokine and antioxidant levels in peripheral blood; decreases oxidative stress and low-grade (Panza et al., 2018).

Decreases body weight gain and high-fat diets; reduces plasma triglycerides and creatinine levels; increases liver expression of lipogenesis-related genes (Uecker et al., 2019).

Antioxidant and anti-inflammatory properties; glucose reduction and improvement of insulin sensitivity; glycaemic control; with antihyperglycaemic, antiobesity and antihyperlipidaemic effects (Habtemarian, 2019).

humans / mice / *Caenorhabditis elegans* / reviews

Figure 6 – Some potential health benefits associated with yerba-mate consumption (in vitro and vivo tests)

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3 PERFORMANCE OF YERBA MATE UNDER DIFFERENT PRODUCTION SYSTEMS

Article formatted for the International Journal of Agricultural and Biological Engineering

Abstract: Species *Ilex paraguariensis* A. St-Hil. is a great natural wealth, since it has considerable economic value and many use possibilities. Thus, in order to better understand the dynamics of yerba mate cultivation, the present study aimed to characterize the agronomic performance of the species when produced in different seasons and production systems, as well as to recognize the interference of cultivation conditions in the biochemical composition of its leaves. Ultimately, this study intended to recommend suitable cultivation conditions and harvesting time to obtain higher-quality raw material. Three cultivation systems were evaluated (*I. paraguariensis* in native forest - NF, *I. paraguariensis* planted in open forest - OF and *I. paraguariensis* planted in full sun - FS) in two harvest seasons (summer and winter). Systems were evaluated according to their production, phenology and physicochemical composition of leaves. Results showed that cultivation systems affect *I. paraguariensis* production and composition, as well as the the harvest seasons. OF production system appears to be more promising as it shows better quality and productivity and higher concentrations of caffeine, flavonoids, 3-CQA and 5-CQA, as well as the highest DPPH radical scavenging capacity. Winter harvest presented leaves with higher concentration of minerals (Ca, Mg, Mn, Fe, Zn and B), methylxanthines, phenolic compounds and antioxidant activity.

Keywords: *Ilex paraguariensis* A. St-Hil.; Mate; methylxanthines; phenology; phenolic compounds.

3.1 INTRODUCTION

Species *I. paraguariensis* has area of occurrence of approximately 540,000 km² covering subtropical and temperate regions of South America in Brazil, Argentina and Paraguay. It is a great natural wealth, since it has considerable economic value and importance in the agricultural production systems, generating income and frequently playing a strategic role in the preservation of forest areas combined with the multiple uses of natural resources [1-3].

It is economically exploited for a variety of uses such as infusions (tea, *tereré* and *chimarrão*, widely consumed in Latin America), energy drinks and extracts with application in pharmaceutical and nutraceutical industries (popular in countries in North America, Europe and Asia) [4,5,3].

Its chemical composition is unique and versatile, including compounds such as vitamins, minerals, flavonoids, phenolic acids, saponins and methylxanthines, responsible for numerous health benefits as stimulant and antioxidant. Consequently, the growing demand for high-quality products with therapeutic characteristics results in market opportunities that can be better used by *I. paraguariensis* producers [6-7].

I. paraguariensis production systems generally present great plurality in relation to the adaptability of the species to different luminosity levels and management to which they are submitted, configuring several productive designs. Among them, *I. paraguariensis* planted under shadow (managed in native forests or forest remnants with different degrees of canopy opening and *I. paraguariensis* densification) and *I. paraguariensis* planted in full sun (in single cultivation, without shading) stand out [8,2,9,3].

Genotypes, agronomic and environmental conditions that plants are submitted affect their chemical composition and potential biological effects. Some studies have shown that changes in light intensity during *I. paraguariensis* cultivation can promote the accumulation of certain compounds. In this context, there is the perspective of producing raw material with special quality characteristics such as high concentration of chemical compounds and improved aroma and flavor in order to compete in commercial circuits of the world market [10,3].

However, there are many factors that can act in its composition and most studies do not present results that can be considered definitive, particularly regarding quantitative determinations and their correlation with production variables[11]. To our knowledge, the quality of the raw material produced in each of these production systems is unknown. This information will give the industry indications of the best system for each *I. paraguariensis* byproduct. In addition, new studies will support the association between health, *I. paraguariensis* consumption and the maintenance of sustainable supply chains with forest preservation [12,13,14,10].

Aiming to subsidize the understanding of the dynamics of yerba mate cultivation, the present study aimed to characterize the agronomic performance of the species when produced in different seasons and production systems, as well as to analyze the interference of cultivation conditions in the composition biochemistry of its leaves. Ultimately, this study intended to recommend suitable cultivation conditions and harvest seasons to obtain higher quality raw material.

3.2 MATERIAL AND METHODS

3.2.1 Study area and production systems

This research was carried out in three *I. paraguariensis* production areas located in the “Planalto Norte Catarinense” region, municipalities of Três Barras (26°23'23.58"S and 50°16'9.15"W, 810 m a.s.l.) and Papanduva (26°12 '15.33"S and 50°14'26.87"W, 818 m a.s.l.; 26°23'37.55"S and 50°16'27.88"W, 814 m a.s.l.). According to the Köppen classification, the climate of the region is of Cfb type, described as temperate with mild summer. The vegetation is found in the Montane Araucaria Forest domain in the Atlantic Forest biome[15]. Temperature and rainfall conditions were obtained from the ‘Centro de Informações de Recursos Ambientais e de Hidrometeorologia de Santa Catarina’ Meteorological Stations located at Papanduva and Três Barras.

Three *I. paraguariensis* production systems were studied in this research (Figure 1). According to the classification of Marques [2], these systems can be described as:

- *I. paraguariensis* exploited in native forest (NF) - forest physiognomy with high degree of conservation (forest coverage index (ICF) between 16.0 and 19.0, usually reaching the advanced regeneration stage and production from native trees). In this system, a high diversity of native species was observed, among them araucaria, bracatinga, cinnamon, cedar, cow foot, imbuia, despite the lower density of yerba mate plants. All plants were native to the area;
- *I. paraguariensis* planted in open forest (OF) - landscape characterized by forest physiognomy at intermediate conservation stage (ICF between 8.5 and 13.5), production from planted trees that represent more than 50% of the total production of the area. The seedlings came from sexual propagation in regional nurseries;
- *I. paraguariensis* planted in full sun (FS) - landscape unit characterized by planted trees, usually with perceptible alignment, without shading provided by other trees. The planting spacing was 2.0 x 2.0. The seedlings came from sexual propagation in regional nurseries.

All plants had more than five years of production and were evaluated in the years 2017 and 2018 in the summer and winter seasons.

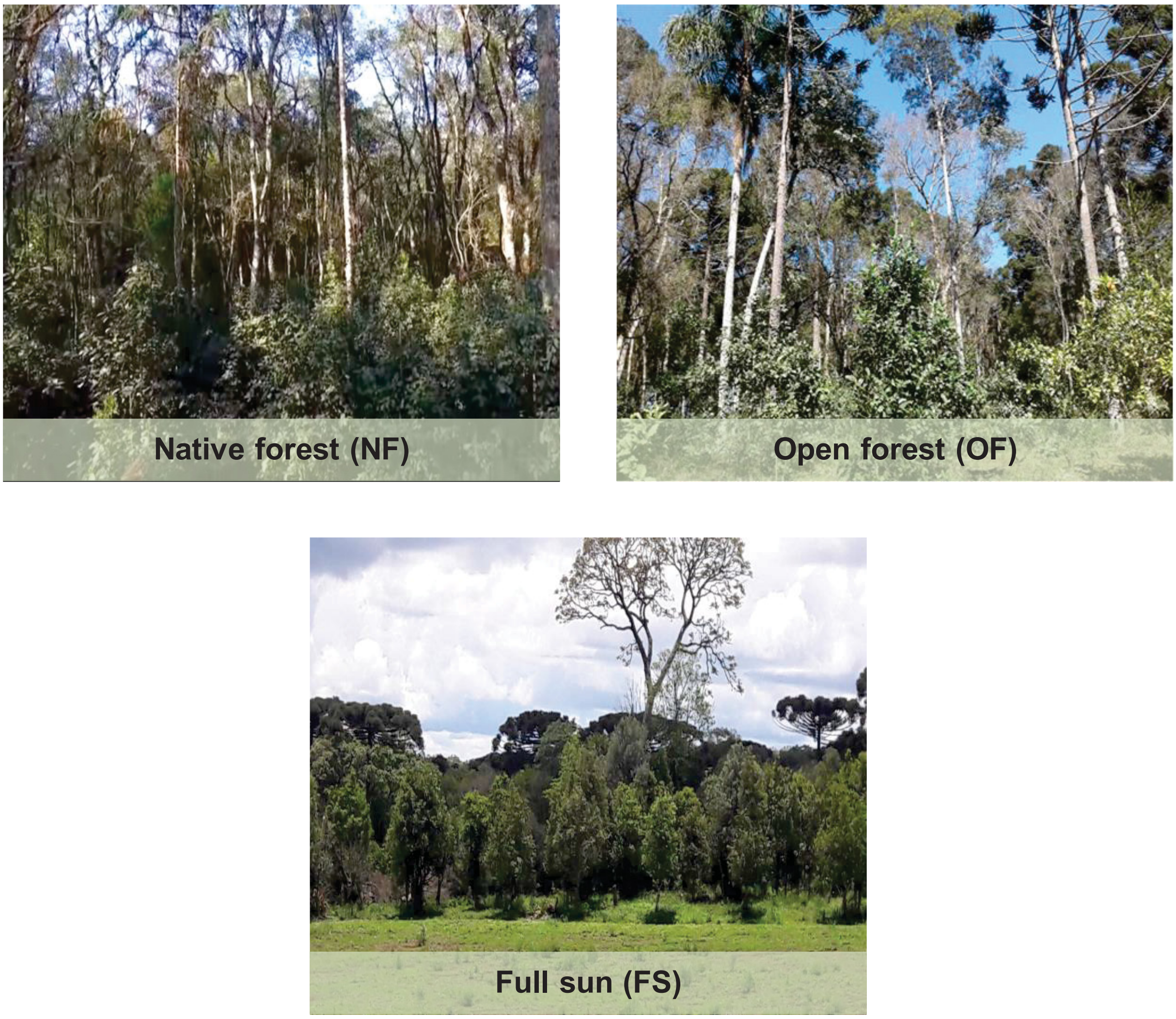

FIGURE 1 – *I. paraguariensis* production systems studied in this research (classification of Marques [2]).

3.2.2 Characterization of production systems

Systems characteristics (luminosity, height, diameter at breast height - DBH and plant density) were quantified in each area by sampling 8 individuals in ten plots of 16 m x 16 m. Average productivity, phenology and the physicochemical properties of leaves were quantified in both seasons by dividing each plot into four 8 m x 8 m subplots, with 20 of them being randomly drawn to harvest the green mass, totaling 0.128 ha in each area.

Soil chemical characteristics were evaluated in each of the areas by sampling 40 collection points at depth of 0 to 20 cm (Table 1).

Luminosity was measured in the visible range of the spectrum using digital luximeter (with a 4 cm diameter receiver) for 10 days. On each day, four readings were performed at 1 m from the ground at each collection point: to the north, south, east and west of 80 *I. paraguariensis* trees in each area [16]. Population density was calculated by the total number of individuals divided by the total area of each plot. Diameter at breast height and height of trees were measured using a measuring tape and graduated stick, respectively.

3.2.3 Phenology and production

Plants were biweekly evaluated in the 2017/2018 and 2018/2019 cycles between August and March, covering the reproductive period from the emission of flower buds to the fruit ripening. In these evaluations, phenophases of flower buds, open flowers, immature green fruits and ripe fruits (red and black skin color) were recorded [4]. Average production per plant and estimated productivity per hectare ($t.ha^{-1}$) were evaluated in the summer (December 2017) and winter seasons (August 2018) based on plant density per plot and fresh leaf mass.

3.2.4 Physicochemical properties

Branches were collected from the middle portion of trees at three points in the canopy on three trees in each sub-plot for analysis of the physicochemical properties, always using full leaves (leaf blade + petiole) from the middle portion of the year sprout, choosing entire branches of intermediate growth. To measure leaf area and color, a branch from each tree was used, totaling 60 branches per area and 3 leaves per branch. For analysis of minerals and bioactive compounds, total collected leaves were divided: 1/3 for quantification of minerals and 2/3 for quantification of bioactive compounds.

Leaves were separated and linearly measured with the aid of a ruler and the leaf area was calculated using the following equation: $AF = 0.35632 + 0.62125 (LxA)$, with r Pearson = 0.9703, where L is equal to the longitudinal diameter and A is the equatorial diameter of leaves, according to methodology of Skromeda et al [17]. The color of leaves was determined with the aid of digital colorimeter, which evaluated the color difference between samples. The parameters used were L *, a * and b *, and the hue of samples was determined from the ratio between b * and a *.

TABLE 1 - Chemical attributes of soils in the 0-20 layer in the different yerba mate production systems, 2018/2019 harvest season. (NF - *I. paraguariensis* planted in native forest; OF - *I. paraguariensis* planted in open forest; FS - *I. paraguariensis* planted in full sun).

	NF	OF	FS
Clay (%)	46.0	35.0	56.0
pH – (H_2O)	3.8	3.8	4.5
Organic matter (%)	5.1	3.8	4.7
P (mg/dm³)	5.8	3.6	2.4
Al (cmolc/dm³)	5.4	4.2	4.9
Ca (cmolc/dm³)	1.9	0.5	1.3
K (cmolc/dm³)	0.4	0.2	0.2
Mg (cmolc/dm³)	0.5	0.3	1.0
H + Al (cmolc/dm³)	34.5	24.0	20.5
Exchangeable cátions pH 7.0 (cmolc/dm³)	37.3	25.0	23.0
Al saturation (%)	65.9	81.4	66.2

Source: EPAGRI Soil Analysis Laboratory.

To determine the mineral content in complete leaves (leaf blade + petiole) from the middle portion of the year shoot, the following procedure was adopted: decontamination of the leaf surface, drying, grinding, weighing, sample digestion and dosages of nutrients nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), copper (Cu), zinc (Zn), manganese (Mn) and boron (B), according to methodology of Schweitzer and Zuzuki [18].

To determine secondary metabolism compounds, leaves were dried in microwave oven operating at 2450 MHz until reaching constant weight, being later ground in processor. For analysis of phenolic compounds (total polyphenols and flavonoids) and antioxidant activity, samples were extracted with water at 80ºC and 70% methanol, according to methodology of Heck et al. [19] and Gullón et al [7].

Total phenolic compounds were determined using the Folin-Ciocalteu solution, with spectrophotometric reading at wavelength of 725 nm and results expressed in mg of gallic acid equivalent (GAE) [10]. Flavonoids total content were also quantified by the spectrophotometric method and results were expressed in mg of quercetin equivalent (QE) [20].

To quantify the antioxidant activity, the kinetic reaction between antioxidants present in the sample and the DPPH radical was used, according to methodology of Jeszka-Skowron et al [21]. The free radical scavenging capacity was estimated by the equation: % radical scavenging = ((Abs control – Abs sample) / (Abs control)) x 100, where Abs is the absorbance. The iron reduction power (FRAP) is another method used to determine the antioxidant activity, according to Zhu et al [22], with some modifications. Results were expressed in mg. GAE-^{1} (gallic acid equivalent).

Caffeine, theobromine, monocaffeoylquinic acid (3 - caffeoylquinic acid (3-CQA), 4 - caffeoylquinic acid (4-CQA), 5 - caffeoylquinic acid (5-CQA)) were quantification with 10 mg of sample weighed, diluted and homogenized in 50% ethanol. Extraction was performed in Thermomixer for 1 h at 60ºC at 450 rpm. Subsequently, extracts were centrifuged, filtered and packed in vial for HPLC analysis. Umbelliferone 50 µg.mL^{-1} internal standard was added for quality control. Chromatographic analyses were performed using Shimadzu® liquid chromatograph (UFLC), controlled by the LC Solution software and equipped with automatic injector and UV detector (SPD-20A). Compounds detection was performed at fixed wavelength of 280 nm. Results were expressed in mg of compound per g of sample (mg.g^{-1}) (dry basis).

3.2.5 Statistical analysis

For all data, analysis of variance (ANOVA) was performed and when significant, was followed by comparison of means by the Tukey test with $p \leq 0.05$. Correlation calculations, using Pearson's coefficient, were performed for the chemical compounds of leaves.

3.3 RESULTS

The presence of acidic soils, accumulation of organic matter in superficial horizons and very low percentage of base saturation in the three study areas was observed (Table 1).

Areas also showed similar temperature and rainfall (Figure 2). Rainfall distribution was irregular in the region, and months with the lowest accumulated rainfall were July / 2017, April / 2018 and July / 2018 (Figure 1), a time when yerba mate plants are in the vegetative phase and little growth is observed due to low winter temperatures. Accumulated rainfall was 2629.6 mm.year^{-1} in NF and FS systems and, 2808.6 mm.year^{-1} in the OF system, and the average value was 2719.1 mm.year^{-1}. Higher rainfall accumulations were observed in January and October, with emphasis on the month of October 2018, where rainfall accumulation in regions was greater than 300 mm. Greater temperature increase occurred between November and February and significant decreases between May and August in the years 2017 and 2018, composing very different harvest seasons in terms of climatic characteristics (Figure 2).

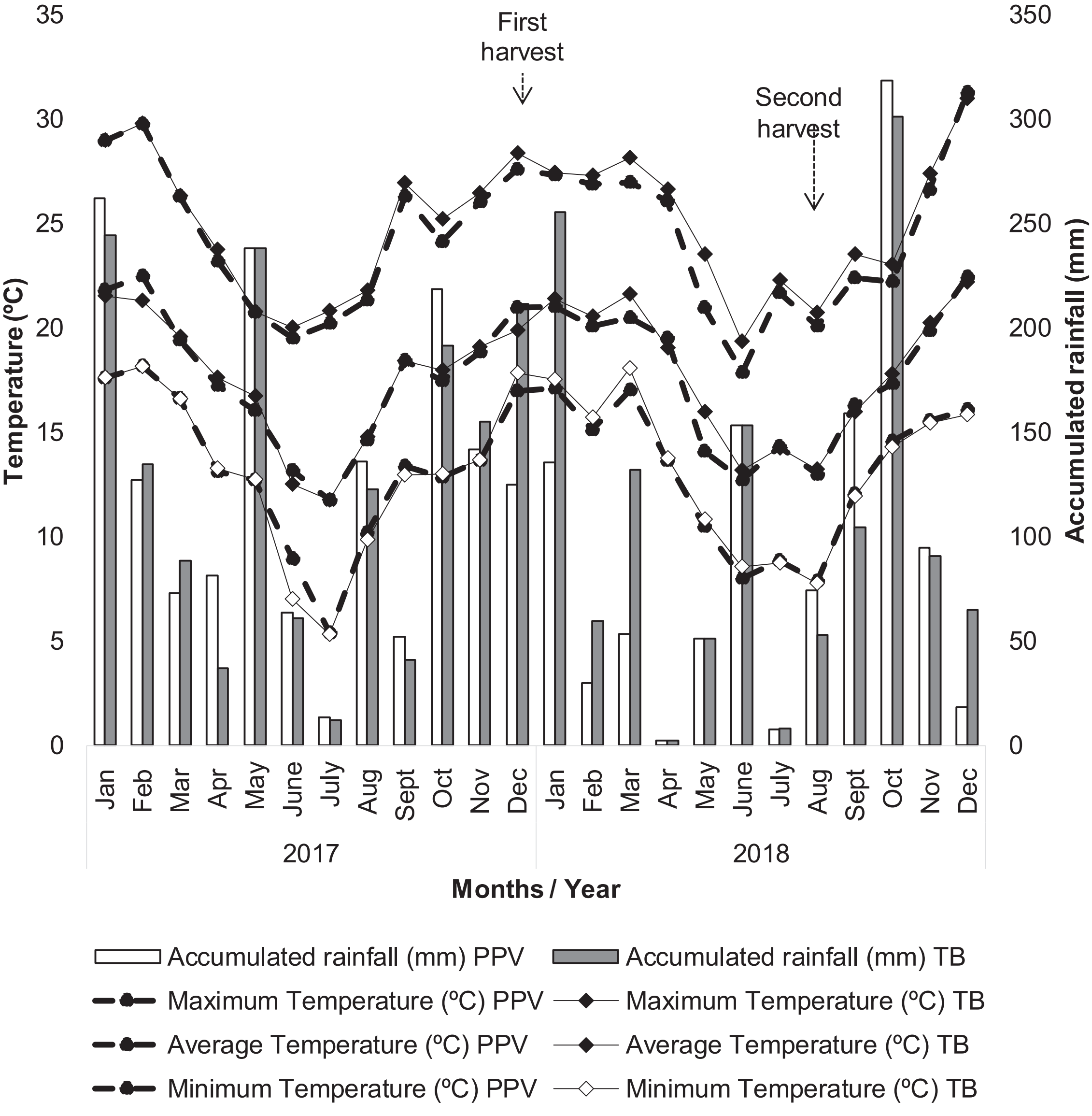

FIGURE 2 - Climatic characteristics of the years 2017 and 2018, Papanduva (PPV) and Três Barras (TB) - SC. Data were obtained from Papanduva (PPV) and Três Barras (TB) Meteorological Stations. Source: EPAGRI / CIRAM (2017 and 2018).

Regarding the microclimatic characteristics, the luminosity of the FS area in relation to OF and NF areas was approximately four and ten times greater, respectively (Table 2). The system with the largest number of plants per area is FS. The OF system has intermediate canopy density and opening among systems. The highest productivity per area is found in FS, but the highest production per plant is found in the other systems due to the presence of taller trees, usually with greater green mass.

TABLE 2 - Luminosity and productive characteristics of the different *I. paraguariensis* production systems, 2018/2019 harvest season (NF: *I. paraguariensis* planted in native forest; OF: *I. paraguariensis* planted in open forest; FS: *I. paraguariensis* planted in full sun).

	Illuminance Lux ($lm.m^{-2}$)	Plant density ($ind.ha^{-1}$)	Production ($kg.plant^{-1}$)	Productivity ($t.ha^{-1}$)	Height (m)	Breast height diameter (cm)
NF	68.16a	635.00a	8.29a	5.26c	3.39a	10.43b
OF	184.52b	1181.00b	8.18a	9.66b	2.40b	9.25b
FS	708.16c	2500.00c	6.10b	15.25a	1.88c	13.65a
CV %	23.28	21.14	7.02	7.02	21.12	22.87

Averages followed by the same letter do not differ statistically at the Tukey Test at 5% probability level. CV% = Coefficient of variation.

Reproductive period of the species in the FS area was similar in the two years of evaluation, with average duration of five months, and the succession of phenological phases was a consequence of climatic conditions, mainly of the increase in temperature and accumulated rainfall. In both years, flowering followed by fruiting was observed only in FS (Figure 3). The flower bud phase occurred between July and August (when temperatures and rainfall started to increase); flower opening and pollination occurred between August and September, green fruits occurred between September and November, and fruit maturation between November to February.

Figure 4A shows leaf size and leaf area characteristics. Larger leaf areas were found for NF and OF systems in both seasons. Regarding leaf color, greener and brighter leaves are observed in the OF system, followed by the NF system in both seasons (Figure 4B).

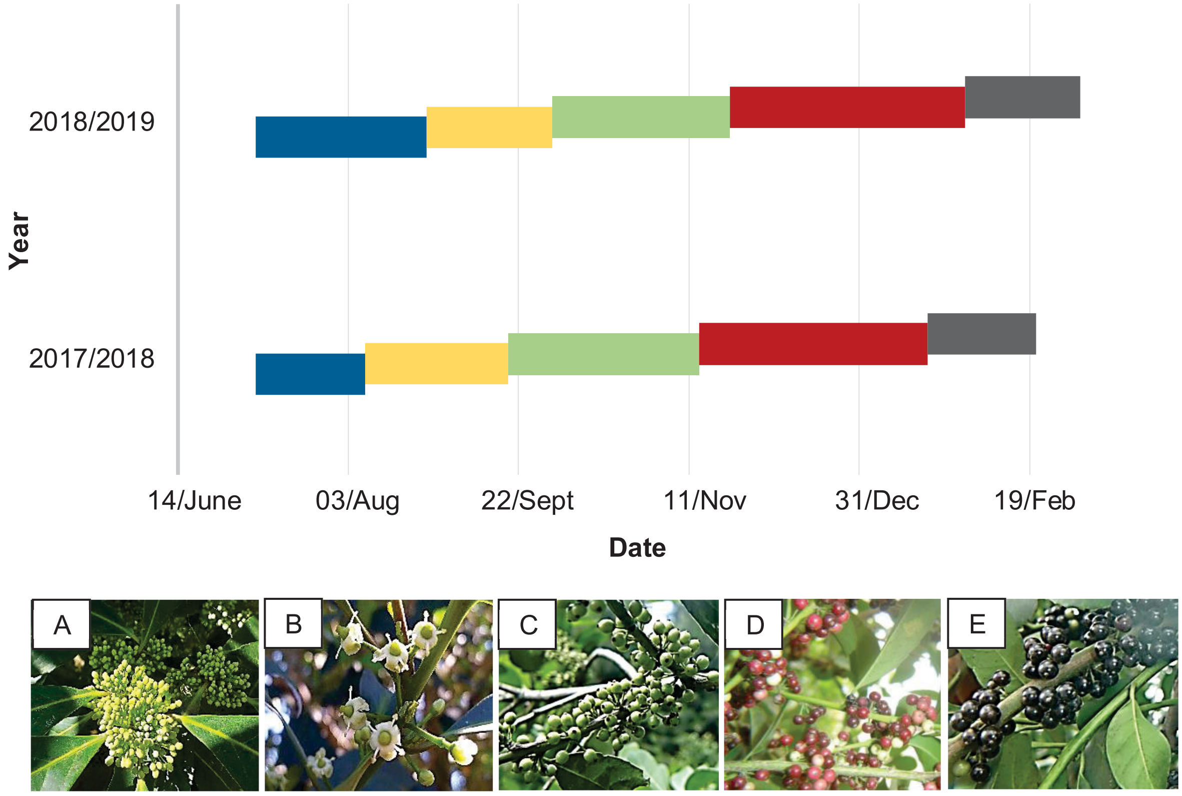

FIGURE 3 - Flowering and fruiting observed in *I. paraguariensis* grown in full sun. (A - Flower buds 🟦; B - open flowers 🟨; C - Green fruits (immature) 🟩; D – Red fruits 🟥 ; E - Purple fruits ⬛). Photos credit: Gilberto Neppel, 2019.

Leaves nutrient content were different in each season and among *I. paraguariensis* production systems (Figure 5). Concentration sequence observed for macronutrients was N> K> Ca> Mg> P. N and K levels were generally lower in the area with the highest shading level, with no significance only for the K content in the winter harvest. Higher N concentration was observed in the OF system and for the K content in the FS system in the summer harvest. Regarding the phosphorus content found in leaves, there was variation only in the summer harvest and in the NF area with the lowest leaf content, even though this area was the one with the highest soil P content among areas under study (Table 1 and Figure 4A).

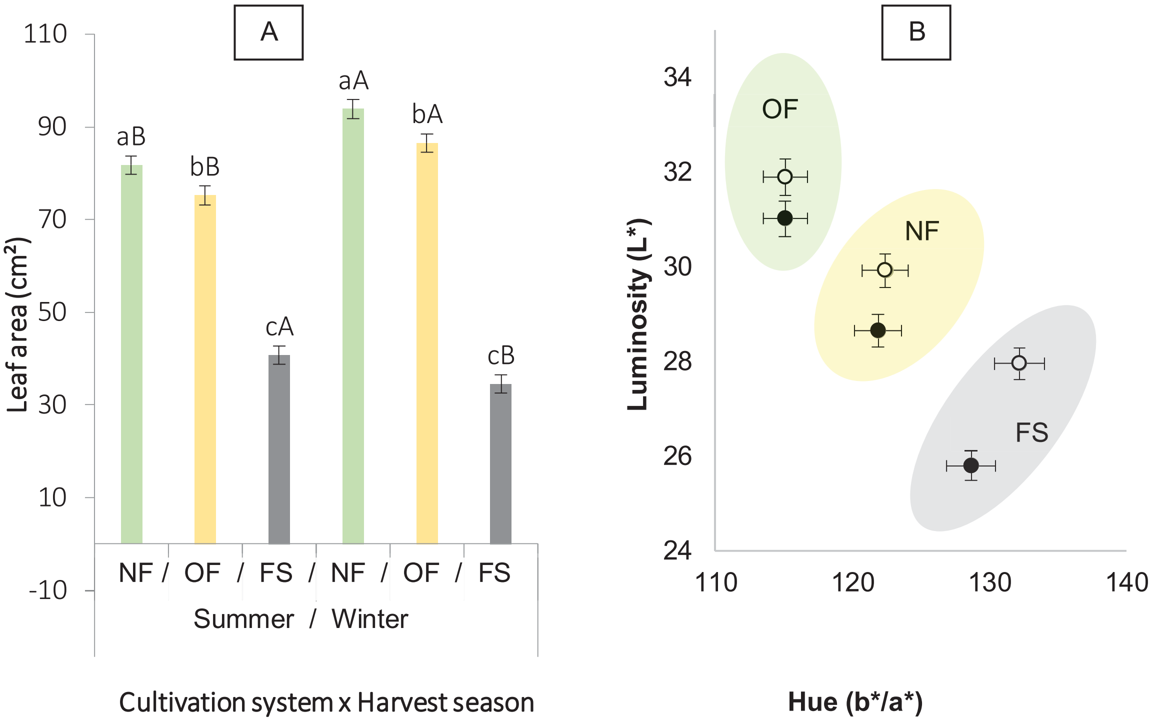

FIGURE 4 - Physical characterization of *I. paraguariensis* leaves according to the harvest season (winter and summer) and cultivation system (NF: *I. paraguariensis* planted in native forest; OF: *I. paraguariensis* planted in open forest; FS: *I. paraguariensis* planted in full sun). (A - leaf area and B - leaf color; bar indicates the standard deviation (Summer ○; Winter ●). Lower case letters indicate differences between cultivation systems. Upper case letters indicate differences between seasons.

On the other hand, higher Ca and Mg accumulations were observed in the winter harvest (Figure 5A). Regarding the cultivation system, all were different from each other in relation to the Ca content, and lower values were found in the FS system. For Mg, the largest accumulation occurred in the NF system and the lowest in the OF system.

All micronutrients, except Zn, showed higher concentration during the winter, and in general, its also occurred the NF system (Figure 5B). Micronutrient concentration in *I. paraguariensis* leaves was Mn> Fe> Zn> B> Cu. The greatest variation observed among micronutrients occurred for Mn in relation to seasons.

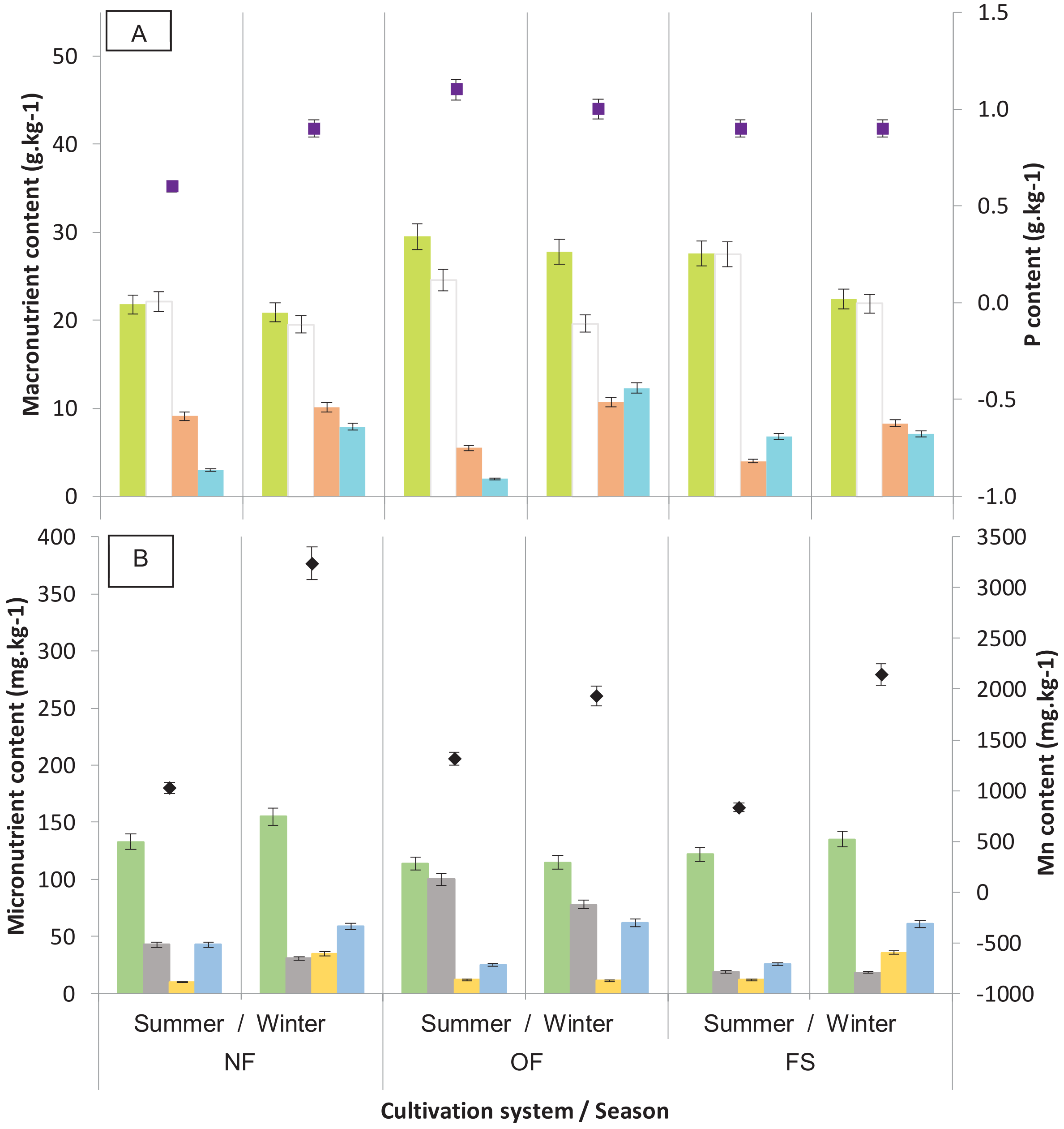

FIGURE 5 - *I. paraguariensis* leaves nutritional content from three cultivation systems (NF: native forest; OF: planted in open forest; FS: planted in full sun) and two seasons (summer 2017; winter 2018). (A - macronutrients in g.kg^{-1} (N 🟩 ; P ■ ; K ☐ ; Ca 🟧 ; Mg 🟦) and B – micronutrients in mg.kg^{-1} (Fe 🟩; Mn ◆ ; Zn ■; Cu 🟨; B 🟦)). (Average contents and standard deviation)

The levels of methylxanthines depend simultaneously on systems and seasons (Table 3). The highest caffeine production was in the OF system with no difference between seasons, which presented the lowest theobromine content in the winter harvest. Higher theobromine content was observed in the NF system in the winter harvest.

TABLE 3 - Methylxanthines, phenolic compounds and antioxidant activity in *I. paraguariensis* leaves in three cultivation systems (NF: native forest; OF: open forest; FS: planted in full sun) and two different seasons (summer and winter).

	Caffeine (mg.g^{-1})		Theobromine (mg.g^{-1})	
	Summer	Winter	Summer	Winter
NF	11.98bA	13.11cA	1.23cB	9.32aA
OF	19.42aA	18.78aA	2.33bB	3.00cA
FS	11.50bB	15.24bA	4.68aA	5.24bA
CV% syst/sea	3.61	6.85	4.52	7.05
	Phenolic compounds (mg EAG.g^{-1})		Flavonoids (mg EQ.g^{-1})	
	Summer	Winter	Summer	Winter
NF	89.41aA	84.06aB	5.45aA	2.26cB
OF	79.78bA	83.06aA	3.25bB	4.38aA
FS	74.32cB	85.42aA	2.29cA	3.10bA
CV% syst/sea	2.04	2.03	8.74	12.81
	3 - CQA (mg.g^{-1})		4 - CQA (mg.g^{-1})	
	Summer	Winter	Summer	Winter
NF	7.86bA	8.36aA	7.05aA	7.03aA
OF	9.97aA	6.33bB	4.74bB	6.96aA
FS	6.32cB	8.64aA	4.09bB	5.87bA
CV% syst/sea	2.44	6.75	3.23	6.41
		5 - CQA (mg.g^{-1})		
		Summer	Winter	
	NF	15.26bB	21.63aA	
	OF	22.25aA	16.89cB	
	FS	21.29aA	19.40bA	
	CV% syst/sea	0.95	6.25	
	DPPH (%)		FRAP (mg EAG.g^{-1}) ns	
	Summer	Winter	Summer	Winter
NF	73.03aA	67.79bB	106.27	101.90
OF	67.25bB	78.96aA	103.17	103.34
FS	65.45bB	76.00aA	103.05	107.30
CV% syst/sea	2.95	2.38	1.78	2.35

Averages followed by the same lowercase letter in column and uppercase in the row do not differ statistically at the Tukey Test at 5% probability level. CV% = Coefficient of variation in %. Syst - system factor and Sea - season fator.

Results for the contents of total phenolic compounds, flavonoids and caffeoylquinic acids in *I. paraguariensist* leaves also indicated differences between seasons and production systems (Table 3). Shaded areas, in the summer harvest, in general, produced more phenolic compounds. Gradual reduction in the content of total phenolic compounds and flavonoids in the different cultivation systems (NF > OF > FS) was observed in the summer harvest. Regarding the 5-caffeolquinic compound content (major isomer of caffeoylquinic acids), OF and FS systems showed average increase of 29.9% when compared to NF. The opposite occurred in the winter harvest.

Two chemical tests were used for the *in vitro* evaluation of the antioxidant activity of samples. The FRAP method is based on the production of Fe^{2+} ion from the reduction of Fe^{3+} ion. The higher the concentration of antioxidants in the sample, the greater the reduction due to its property of binding to this metal. In this sense, there was no variation in relation to season and cultivation system. Regarding the antioxidant activity evaluated by the DPPH method, there were variations between seasons and systems, with higher values for NF in the summer and, in the winter, the opposite.

Correlation analyses were performed for compounds present in *I. paraguariensis* leaves (Table 4). Strong positive correlations were found for theobromine with Fe, Mn and Cu; caffeine with Zn; 4 - CQA with Ca and B; 5 - CQA with P; total polyphenols with DPPH; flavonoids with DPPH; Ca with B; Mg with B; Fe with Mn and Cu; and Zn and Cu. Strong negative correlations were observed for K with 4 - CQA, Ca, and B; DPPH with Mg; and N with Fe.

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TABLE 4 - Correlation values by the Pearson's coefficient (ρ) of biochemical compounds of *I. paraguariensis* leaves produced in three cultivation systems (NF: native forest; OF: planted in open forest; FS: planted in full sun) and two crops (summer and winter).

	Theobromine	**Caffeine**	**3 - CQA**	**4 - CQA**	**5 - CQA**	**Phenols**	**Flavonoids**	**DPPH**	**FRAP**	**N**	**P**	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
Theobromine	**1.00**																		
Caffeine	-0.28	**1.00**																	
3 - CQA	0.03	0.35	**1.00**																
4 - CQA	0.13	0.01	-0.04	**1.00**															
5 - CQA	0.54	0.14	0.42	-0.56	**1.00**														
Phenols	-0.33	-0.22	-0.22	-0.38	0.10	**1.00**													
Flavonoids	-0.52	0.11	0.33	0.05	-0.14	0.54	**1.00**												
DPPH	-0.62	-0.15	0.14	-0.43	-0.03	0.77	0.70	**1.00**											
FRAP	0.00	-0.39	-0.33	-0.45	0.12	0.34	0.13	0.22	**1.00**										
N	-0.49	0.55	-0.19	-0.65	0.21	0.39	0.09	0.31	0.24	**1.00**									
P	0.41	0.42	0.14	-0.32	0.70	0.16	-0.12	-0.17	0.16	0.41	**1.00**								
K	0.02	-0.49	0.26	-0.72	0.50	0.44	0.11	0.58	0.39	0.05	-0.01	**1.00**							
Ca	0.13	0.17	-0.10	0.94	-0.57	-0.49	-0.08	-0.55	-0.53	-0.51	-0.23	-0.86	**1.00**						
Mg	0.30	0.19	-0.63	0.41	-0.25	-0.38	-0.51	-0.76	-0.05	0.05	0.18	-0.79	0.58	**1.00**					
Fe	0.76	-0.35	0.20	0.36	0.19	-0.37	-0.39	-0.49	-0.25	-0.74	0.10	-0.01	0.35	0.12	**1.00**				
Mn	0.84	0.03	0.22	0.52	0.26	-0.55	-0.35	-0.72	-0.33	-0.60	0.33	-0.39	0.57	0.40	0.77	**1.00**			
Zn	-0.52	0.82	0.30	0.01	0.00	0.23	0.53	0.32	-0.29	0.56	0.31	-0.34	0.10	-0.06	-0.52	-0.19	**1.00**		
Cu	0.80	-0.16	0.33	0.20	0.36	-0.69	-0.60	-0.69	-0.18	-0.61	0.19	0.00	0.22	0.14	0.84	0.79	-0.53	**1.00**	
B	0.34	0.01	-0.27	0.80	-0.48	-0.66	-0.47	-0.80	-0.37	-0.52	-0.18	-0.77	0.88	0.74	0.51	0.62	-0.24	0.47	**1.00**

Positive values indicate positive correlation. Negative values indicate negative correlation. $\rho > 0.9$ indicates very strong correlation; $0.89 > \rho > 0.70$ indicates strong correlation; $0.69 > \rho > 0.40$ indicates moderate correlation; $\rho < 0.39$ indicates weak or absent correlation. Gray: strong to very strong positive correlation. White with outline: strong negative correlation.

3.4 DISCUSSION

The average *I. paraguariensis* productivity in Brazil (area with the greatest coverage of the species) is 8.2 t.ha^{-1}, while in research areas, with the adoption of technologies such as strategic pruning management (formation and conduction), fertilization and biological pest control, this value has been higher than 18 t.ha^{-1}, reaching maximum of 35 t.ha^{-1} [23,24]. In this study, productivity ranged from 5.26 (NF) to 15.25 t. ha^{-1} (FS), which demonstrates that the productive potential of the species can be further exploited. NF and OF systems showed the highest yields per plant due to higher average heights and leaf areas, in contrast to lower yields per area due to the lower planting density. However, productivity in the OF area was higher than the Brazilian average, with the possibility of being increased with the use of better management, as reported in research areas [23,24].

Although the higher density of yerba mate plants has been shown in the FS area, in other systems there is greater interspecific competition due to the presence of other trees in the place, often providing greater density for yerba mate plants.

Luminosity directly affects the physiological and morphological behavior of plants and, consequently, their productivity response. The largest leaf areas and the darkest leaves occurred in NF and OF systems. Generally, plants increase their photosynthetic area when in shading conditions to produce the energy necessary for their survival [25]. Higher leaf area levels are related to higher productions per plant. Boeger et al. [26] studied 4 species native to Montane Araucaria Forest cultivated under 3 light conditions and observed that cultivation with the lowest luminosity (13.83%) was the one that provided the highest biomass production per area unit for all species. Vieira et al. [27] also observed smaller leaf area for *I. paraguariensis* in full sun cultivation, since shade leaves have morphological changes (size, shape, thickness of the wax cover and color) due to their position in relation to the sun [28,29].

The Brazilian market prefers brighter yerba mate leaves with more intense green color, which are considered to be of better quality [30]. This characteristic is found in OF and NF systems (Figure 4B). Lighter colors were produced in the FS system due to the high intensity of solar radiation absorbed by plants [28].

Several studies suggest that shade leaves usually have higher chlorophyll concentration per area unit to increase the absorption of red light, which is limited in dark environments, and to maintain the energy balance between PSII and PSI photosystems [26,29]. The results presented here suggest that *I. paraguariensis* has strategies to adapt to different light conditions: there seems to be more chlorophyll in shade leaves, resulting in more intense green color [27].

Simultaneously, luminosity controls the development of plants, because in addition to providing energy for photosynthesis, it provides signals to the photoreceptors of leaves that regulate their phenology. Thus, the absence of flowering in shaded areas (NF and OF) probably is due to the fact that the production of *I. paraguariensis* fruits is dependent on the condition of exposure to the sun, since light signals control the induction of genes related to flowering [4,25]. In this context, shading in NF and OF areas seems to have caused microclimate changes, suppressing the process of flower induction and differentiation.

It is worth mentioning that the *I. paraguariensis* fruiting, which is a consequence of flowering, has ecological functions for the survival of the species and also provides food for fauna. However, the presence of fruits at the time of summer harvest in areas of full sun, depreciates the commercial value of leaves, and this is one of the reasons for the predominance of harvests in the month of August, a period that precedes the reproductive phase of the species [31]. Thus, areas with shading levels that suppress flowering have the advantage of providing greater options for the harvest period.

Regarding the mineral chemical composition of leaves, variations related to harvest season and production systems were detected (Figure 5), because with growth and development in their cultivation environment, leaves undergo structural, chemical and functional changes in the distribution of nutrients and absorption processes [32]. This is a highly relevant aspect for *I. paraguariensis*, considering the nutritive value of chemical elements and their function within plants as structure builders, constituents of enzymes or enzymatic cofactors, regulating most metabolic processes.

N and K were found in all areas, but in greater amounts in the growing season of the species (summer), when plants present full metabolic activity, corroborating results reported by Mancilla-Leyton et al. [33], who analyzed the N concentration in the leaves of six species and found higher concentrations in the growing season (summer). Bastos et al. [34] also found higher K levels in *I. paraguariensis* leaves in summer compared to winter. The increase in temperature and rainfall that occurred in August probably contributed to increase the diffusion and mass flow rate of ions in root cells, as temperature and water availability accelerate plant metabolism [35].

It is noteworthy that plants grown in higher luminosity rates generally absorb ions more quickly than those kept in low irradiance, since the latter allocate less photoassimilates to roots and have lower transpiration rates [35], which explains the fact that lower N contents have not been observed for the NF system in both seasons and K in the summer harvest, even with the highest levels of these nutrients in soil in relation to the other areas.

Barbosa et al. [36] studied the growth of *I. paraguariensis* clone in response to phosphate fertilization and observed that in the absence of fertilization, leaves showed P values lower than 1 g kg^{-1}, similar to levels found in the present study. According to results of the soil analysis of the different areas (Table 1), phosphate fertilization for correction and maintenance is recommended in the three areas, which may provide production increases [37,38].

Calcium and magnesium differ from other macronutrients because they are cations with divalent base and remain in the ionic form within plants; however, they exhibit widely contrasting characteristics. In addition to the various functions within plant cells, for having low mobility within plants, Ca binds to pectic acid to form the cell walls of the plant tissue. On the other hand, for being mobile and easily transported via phloem, Mg is an essential part of the chlorophyll structure [39]. In this study, the highest green color indexes also accompanied the highest leaf Mg levels. The average leaf Ca and Mg concentrations were comparable to those observed by Oliva et al. [40] in an area covered by the same biome as in this study (average of 11.2 and 5.8 g kg^{-1}, respectively).

The predominance of higher concentrations of micronutrients in the winter harvest was also reported by Bastos et al. [34]. Fe, Mn and Cu, are part of the same group according to their biochemical function. They are involved in redox reactions and sometimes act as enzyme ligands, sometimes as cofactors. Zn is the only micronutrient that remains in the ionic form inside the plant and acts as a constituent of enzymes. In turn, B has structural function as a constituent of the cell wall and plays an important role in cell elongation and nucleic acid metabolism [35,41]. Boron is an element found in high levels in yerba mate leaves when compared to the average content of other plants and was determined as an element of greater solubility in *I. paraguariensis* infusion with high importance in human nutrition [34,42].

Konieczynski et al. [43] found the following sequence of leaf micronutrients Mn> Zn> Fe> Cu. Oliva et al. [40] found average leaf Mn, Fe, Zn, B and Cu levels of 2074, 98.3, 15.3, 170 and 11.8 $mg.kg^{-1}$ in cultivation in Montane Araucaria Forest, confirming the presence of higher Mn levels and lower Cu levels in the leaves of this species. Mn values in *I. paraguariensis* leaves vary from 346 to 3330 $mg\ kg^{-1}$, but toxicity symptoms were not observed, indicating that this plant has some tolerance mechanism [40,36,42].

Regarding the presence of methylxanthines, other studies confirm levels from 7.10 to 32.23 $mg.g^{-1}$ of caffeine and from 1.12 to 4.38 $mg.g^{-1}$ of theobromine [44,45,43,46]. Tolessa et al. [50] studied the interference of luminosity and altitude in the caffeine content and observed that, at average altitude, the level of intermediate shading also produced higher caffeine levels in coffee grains harvested in mid-December.

Methylxanthines are nitrogenous alkaloids used by plants for their adaptation in the cultivation environment. Their formation occurs mainly from xanthosine, with subsequent action of enzymes theobromine synthase and caffeine synthase. Following the metabolic route, there is formation of 7-methylxanthine, theobromine, and caffeine, after a methylation reaction [47,48,49,41]. Therefore, theobromine is an intermediate compound in the metabolic route of caffeine and, therefore, higher caffeine concentrations were found in the OF area, differently from theobromine (lower levels in this area).

These results may be due to changes in the synthesis of methylxanthines, or just to the interconversion between theobromine and caffeine. If we look at the sum of caffeine and theobromine in winter, we can see that there are no apparent differences between the synthesis of compounds in the different areas. However, if we compare the sum of winter with the summer season, in the NF and FS areas, the value is lower, indicating that from summer to winter there is a new synthesis of methylxanthines in these areas (Table 3).

Regarding the harvest season, Pavarini et al. [51] reported variations in the levels of alkaloids with accumulation of high levels in the winter harvest. Yin et al. [48] also reported greater accumulation in the winter. In addition, Suzuki and Takashi [52] reported a stimulus in the enzymatic activity in the caffeine route in the presence of Mg^{+2}, Mn^{+2} and Ca^{+2}. Interestingly, in the present study, the highest levels of nutrients mentioned above were found in *I. paraguariensis* leaves in the winter, which may have favored the production of these compounds. It is noteworthy that nutrients Fe^{+2}, Mn^{+2} and Cu^{+2} presented strong positive correlation with theobromine and Zn^{+2} strong positive correlation with caffeine, very associated with the role of metal ions as ligands, cofactors or enzymatic constituents (Table 4).

Another important fact is that the N content was higher in the summer harvest (unlike caffeine and theobromine). This is because, in plants, these compounds are also products of N reserve, and there is a storage flow of this nutrient in nitrogenous compounds from summer to winter and, later, a slow degradation according to the plant's need in the growing season [53,48,49,54].

On the other hand, phenolic compounds are synthesized mainly from shikimic acid, where precursors derived from glycolysis and pentose phosphate are converted into aromatic amino acids, more frequently phenylalanine. This group includes hydroxycinnamic acids and flavonoids [55,56]. Hydroxycinnamic acids are often esterified with quinic acid, generically called chlorogenic acids, specifically known as 3 - CQA, 4 - CQA and 5 – CQA [55, 57].

Frizon et al. [58] also observed higher phenolic compounds concentration in shaded areas (intercropped with eucalyptus) comparing to the areas under full sun. Chemically, the main enzyme involved in the synthesis of phenolic compounds is phenylalanine ammonium lyase (FAL). The action of this enzyme is regulated by environmental factors such as temperature and water availability and, it seems to have no association with metal ions [59,55,41,25]. Thus, the intensity and quality of light may have been critical to regulate its metabolic synthesis, which explains the differences found in relation to seasons and cultivation areas.

Positive correlations are reported between cold intensity and duration and RNAm production for FAL and the other key enzymes of the shikimic acid route [60]. Thus, due to lower temperatures, winter had positive effect on the production of total polyphenols and 4 - CQA. In the summer harvest in the FS system, the lowest total polyphenols, flavonoids, 3 - CQA and 4 - CQA values were found. This fact may be related to temperature and luminosity, which due to the absence of shading of plants within this system can reach high values causing oxidation of these compounds. It was also observed that in the summer, plants grown in the FS system were in the fruiting stage. *I. paraguariensense* fruits are rich in phenolic compounds and preferential drains inside the plant [31,41].

Mateos et al. [46] found values of total polyphenols ranging from 76.5 to 84.9 mg GAE.g^{-1} in *I. paraguariensis* samples. Gómez-Juaristiet al. [61] showed average value of 3.3 mg.g^{-1} and Correa et al. [62] found 5.61 mg.g^{-1} for total flavonoid content. In the same context, Butiuk et al. [63] found strong influence of the harvest season on the content of chlorogenic acids and samples collected after the winter season showed substantial reduction in their levels. Meinhart et al. [64] studied 100 plants marketed in Brazil and found the highest content of chlorogenic acids in *I. paraguariensis* leaves among all studied species.

Tolessa et al. [50] also found variations in the levels of chlorogenic acids in coffee grains according to the shading level, as according to the authors, temperature directly influences the production and accumulation of these acids. Correa et al. [62] studied *I. paraguariensis* and also found, among chlorogenic acids, higher 5 - CQA concentration when compared with 3 - CQA and 4 - CQA levels. In turn, Tošovic´ et al. [65] proved the high reactivity of 5 - CQA with free radicals, showing its high antioxidant action.

Thus, flavonoids and chlorogenic acids from *I. paraguariensis* have shown antioxidant activity, acting with different mechanisms such as free radical scavengers or metal chelators [66]. The greater DPPH radical scavenging capacity in the winter is related to the higher concentrations of phenolic compounds in this harvest season.

Furthermore, the variation found for this method indicates that light and temperature conditions of areas directly influence the antioxidant activity of leaves. It summer, where high temperatures occur, the area with the highest radical scavenging % is the one with the lowest luminosity index (FS) (which probably provided a more favorable microclimate for this activity, with milder temperatures inside the forest). In winter, this area becomes the one with the lowest radical scavenging %, also a consequence of lower concentrations of total phenolic compounds and flavonoids (also indicated by strong positive correlation). Regarding the antioxidant activity by the iron reducing power, high values in *I. paraguariensis* leaves were observed, according to other studies [67,68].

3.5 CONCLUSIONS

Cultivation systems affect *I. paraguariensis* production and composition, as well as the harvest seasons.

Open forest production system appears to be promising, due to its high quality and productivity. It also showed the highest concentrations of caffeine, flavonoids, 3-CQA and 5-CQA, together with the highest DPPH radical scavenging capacity.

Winter harvest produced leaves with the highest minerals concentration (Ca, Mg, Mn, Fe, Zn and B), methylxanthines, phenolic compounds and antioxidant activity.

Summer harvest can be an alternative for Native Forest and Open Forest areas, as they also showed some good quality parameters (methylxanthines, phenolic compounds and antioxidant activity). Summer harvest is not recommended for the Full Sun area when the interest is the higher content of leaves chemical compounds.

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4 PHYSICOCHEMICAL CHANGES AND ANTIOXIDANT CAPACITY DURING INDUSTRIAL PROCESSING OF YERBA MATE

Article formatted for the Food and Bioprocess Technology Journal

Abstract

Yerba mate exploitation is based on the use of leaves and branches harvested and submitted to a series of operations that have been little studied. Knowledge of the effect of unit operations on the content of chemical compounds can provide guidance to the industry on how to better conduct processes to reduce losses without affecting quality. Thus, this study aims to characterize physicochemical changes during processing for the production of yerba mate and to evaluate correlations between its compounds and the antioxidant capacity throughout processes. The results showed that the processing is accompanied by changes in color, chemical composition and antioxidant activity. Heat treatment contributed to the greater degradation of green color and chemical compounds. Compounds with the greatest reductions in this operation were phenolic compounds and theobromine.

Keywords: *Ilex paraguariensis*; drying; grinding; storage; methylxanthines; phenolic compounds.

4.1 INTRODUCTION

Commercial exploitation of yerba mate (Ilex paraguariensis) is related to one of the oldest South American industries, which was the activity most involved with the development of this region, preserving its economic and cultural importance today. There are several forms of consumption of its by-products, which has been expanded to Europe, USA and Asia (Olivari et al. 2020; Croge et al. 2021). The global value of this industry is estimated to exceed US$ 2.2 billion, with visible potential increase (FAO 2018; Toresan et al. 2019).

In general terms, yerba mate exploitation is based on the use of leaves and branches, which are harvested, selected and submitted to a series of operations, such as heat treatment for bleaching and drying, grinding and, depending on the case, a storage period, which can result in products with different consumption patterns (Meinhart et al. 2010; Riachi et al. 2018).

After processing, thickly ground yerba mate (*cancheada*) is obtained. This by-product can be used as raw material to produce energy drinks, as an alternative to coffee, widely appreciated for its high content of antioxidants and nutritional compounds. In addition, thickly ground yerba mate has been used as ingredient for gourmet cooking (beers, soft drinks, sweets, cheeses), production of cosmetics with anti-aging function and for the manufacture of functional drinks (juices, kombuchas) (Croge et al. 2021).

Many health benefits have been associated with the consumption of yerba mate such as neuroprotection, antioxidant, anti-inflammatory activities, prevention of degenerative diseases, anti-aging, adjuvant for the treatment of obesity and Parkinson's disease (Gómez-Juaristi et al 2018; Croge et al. 2021). These effects are due to its high content of phenolic compounds, methylxanthines (caffeine and theobromine), saponins, essential oils, vitamins (A, C, B1 and B2) and minerals.

Yerba mate quality is defined by pleasant taste that comprises a balanced combination of bitterness, astringency and sweetness, and is influenced by the different processing stages. The transformation of the fresh raw material into a product ready for infusion preparation represents an effective method to make the product stable for longer. In addition, processing is necessary to make the product more enjoyable for consumption (Berté et al. 2014; Riachi et al. 2018; Croge et al. 2021).

However, the agro-industrial processing of yerba mate has not changed significantly since the beginning of its economic exploitation. In addition, despite the impact of the method on the transformation of the product, there is a general lack of studies related to the effects of processing stages on the physicochemical composition of yerba mate, as the different types of unit operations can result in changes in its composition. The effect of storage on its chemical compounds has not been fully clarified (Dutra et al. 2010; Berté et al. 2014).

Considering the potential for multiple uses of yerba mate and focusing on its chemical compounds, knowledge of the effect of unit operations on the content of each compound can provide guidance to the industry on how to better conduct the process to reduce losses without affecting quality. Thus, this study aimed to characterize physicochemical alterations during yerba mate processing and to evaluate the correlations between its compounds and the antioxidant capacity throughout the processes.

4.2 MATERIALS AND METHODS

4.2.1 Analysis material

The plant material evaluated in this study was composed of leaves and thin branches from yerba mate plants grown in the “Planalto Norte Catarinense” region, Southern Brazil. Shortly after harvest, the material was submitted to the following unit operations to obtain thickly ground yerba mate (Fig. 1): Operation 1 - Heat treatment: bleaching for enzymatic inactivation of the raw material in rotary oven with average temperature of 275 ºC and drying in indirect heat oven equipped with conveyor belt for 12 hours under average temperature of 90º C; Operation 2 - Grinding leaves and branches into medium-sized particles (1.5 to 3 mm) and sieving particles larger than 3 mm; Operation 3 - Storage, also called aging, which consisted of keeping ground leaves and branches protected from light and at room temperature for 120 days (average room temperature in the region in this period ranged from 17.6 to 21.5º C).

4.2.2 Analyses

At the end of each process, 30 subsamples of 300 g each were collected. Each unit operation was developed in duplicate. Subsamples were evaluated for color and subsequently submitted to the extraction process for chemical characterization. Readings for chemical and color tests were performed in triplicate.

4.2.3 Coloring

Color change of yerba mate leaves during unit operations was measured with digital colorimeter using the CIELAB scale, where L * corresponds to luminosity with values from 0 (for absolute black) to 100 (for total white); a * corresponds to coordinates of the horizontal axis measuring primary colors red (+ a *) and green (-a *) with values from 0 to 60; and, the b * expresses coordinates of the vertical axis measuring colors yellow (+ b *) and blue (-b *) with values from 0 to 60 (Santos et al. 2014).

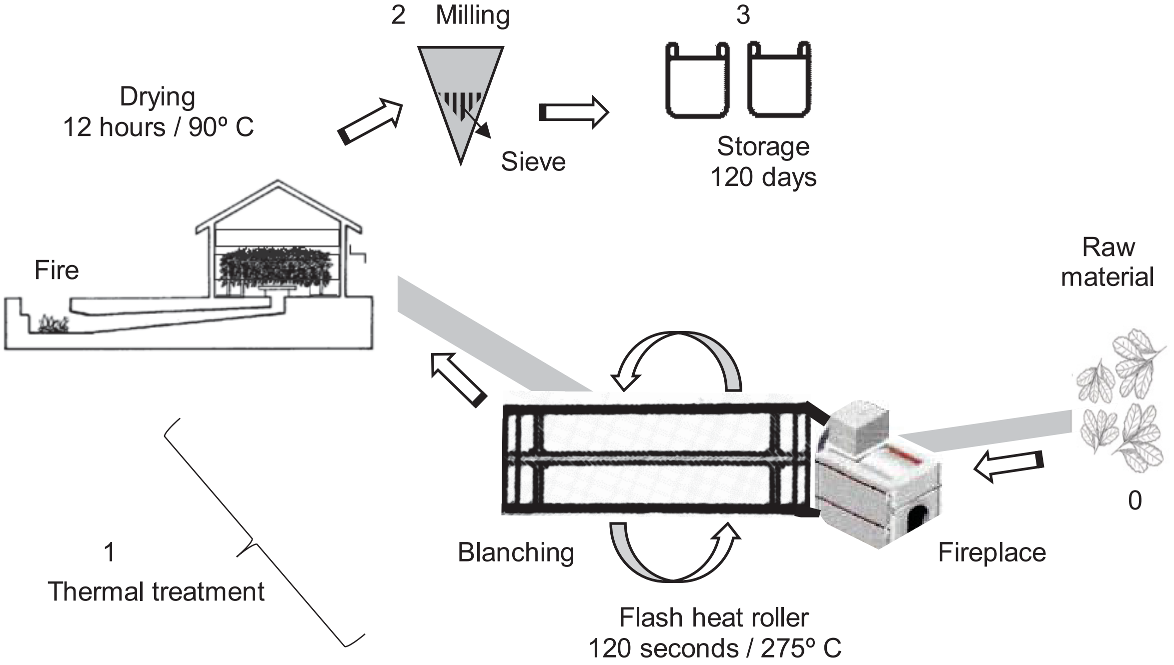


Fig. 1 - Representation of the processing for the production of thickly ground yerba mate. Numbers represent the sampling moments: 0) Raw material; 1) Heat treatment (bleaching and drying); 2) Grinding; 3) Storage for 120 days.

4.2.4 Extraction

The concentration of contents was expressed based on the dry weight and, for that, the moisture content of samples was determined according to the AOAC method (2000) and Frizon et al. (2015). For the extraction of bioactive compounds, 70% methanol was used according to methodology of Heck et al. (2008) and Gullón et al. (2018).

4.2.5 Determination of the phytochemical profile

The total content of phenolic compounds in yerba mate leaves after each unit operation was measured using the Folin-Ciocalteu solution, with spectrophotometric reading at wavelength of 725 nm and results were expressed in mg of gallic acid equivalent (GAE) (Riachi et al. 2018). Content of total flavonoids was quantified by the spectrophotometric method and results were expressed in mg of quercetin equivalent (QE) (Buriol et al. 2009).

Determination of compounds caffeine, theobromine, monocaffeoylquinic acids (3-caffeoylquinic acid (3-CQA), 4 - caffeoylquinic acid (4-CQA), 5 - caffeoylquinic acid

(5-CQA)) was performed using high-performance liquid chromatography (HPLC) adapted from Bravo et al. (2006). Umbeliferone internal standard was used for quality control. The identification of compounds was carried out by comparing the retention times and absorption spectra (between 250 and 400 nm) with those of pure standard compounds (Bravo et al., 2006; Butiuk et al. 2016). Results were expressed in mg of compound per g of sample (mg g^{-1}).

4.2.6 Antioxidant capacity

Kinetic reaction between antioxidants present in sample and ABTS radicals was used to quantify the antioxidant activity, according to methodology of Jeszka-Skowron et al. (2016). The ABTS free radical scavenging capacity was estimated over 7 minutes by the equation: % radical scavenging = ((Abs control - Abs sample) / (Abs control)) x 100, where, Abs is the absorbance.

4.2.7 Experimental design

Analysis of variance (ANOVA) was performed, which when significant, comparison of means was performed by the Tukey test with $p \leq 0.05$.

Represent yerba mate phytochemical profile data was used the Sankey diagram, often used to map the efficiency of production processes in industries. In this diagram, the entry and exit of compounds at each stage of the system becomes visible. The Sankey diagram was built with the NetworkD3 package of the R software. Representation of antioxidant activity data was used the Lattice package to evaluate the time series of the same software.

4.3 RESULTS AND DISCUSSION

Production of thickly ground yerba mate was accompanied by color changes. There was a decrease in green color, followed by increase in yellow color during processing (Fig. 2). The green color is characteristic of yerba mate by-products due to the concentration of chlorophylls. However, thermal processing generally causes the magnesium atoms of their structures to be replaced by hydrogen atoms, producing the so-called pheophytins, which have more yellowish color, close to olive green (Sonar et al. 2019; Acridi et al. 2020).

Heck and Mejia (2007) reported a decrease of up to 80% in chlorophyll concentration during the drying process of yerba mate. Santos et al. (2014) also observed changes in the color of yerba mate according to the type of process. The color change from green to yellow is a requirement of the main import market, Uruguay. However, it is not desired by the Brazilian consumer, for example. In this case, the storage operation is carried out mainly to provide this color change; however, in view of the above, it should be performed only to serve specific markets.

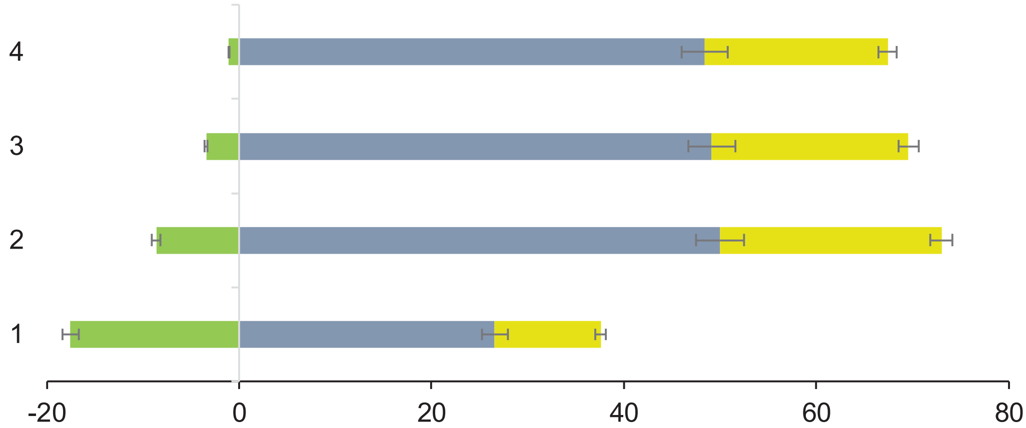
Reduction in green color was accompanied by increase in luminosity, as shown by the L * value, which increased from 26.6 to approximately 50.0 after drying and which, in the following operations, remained constant, indicating that the main factor for bleaching was temperature (Fig. 2).

Results also reveal that the chemical composition of yerba mate varies throughout processing (Fig. 3). The first unit operation to which the raw material is submitted is heat treatment. It begins with bleaching, in which yerba mate is exposed to direct heat of flame obtained with wood combustion. This stage has the function of removing surface moisture and inactivating peroxidase and polyphenoloxidase. These enzymes, if not inactivated, catalyze oxidation reactions of phenolic compounds, causing enzymatic browning, which produces the quality defect called black spots in the final product (Passardi et al. 2006; Damodaran and Parkin 2017).

After the bleaching time, the raw material follows a conveyor attached to the dryer. Among yerba mate production operations, drying is one of the most important, since it is necessary to remove moisture to a point where water activity is low enough to ensure that the product is enzymatically and microbiologically stable. In addition, changes in sensory characteristics occur, making the product more enjoyable for consumption (Chua et al. 2019; Acridi et al. 2020).

However, there are some disadvantages with the heat treatment carried out in this work. This operation leads to changes in chemical composition, which is mainly related to degradation. All concentrations of analyzed compounds decreased (Fig. 3). The degradation of phenolic compounds (58.8%) and theobromine (75.8%) were the highest observed.

Bleaching is a quick and simple treatment, but the lack of control mechanisms in the process makes standardization difficult, which can affect product quality. The drying method used is the exposure of leaves and thin branches to a continuous flow of heated air. Heat is provided and diffuses mainly through conduction. The moisture on the surface of the material is evaporated and removed by the action of forced air movement. At the same time, water is transported from inside the material to its surface driven by a moisture concentration gradient (Chua et al. 2019). Heat and the mass transport process are affected by temperature, air speed and properties of the product to be dried (Wray and Ramaswamy 2015; Chua et al. 2019).



	1	2	3	4
🟦 L*	26.579	49.997	49.137	48.403
🟩 a*	-17.525	-8.623	-3.433	-1.077
🟨 b*	10.994	23.000	20.455	19.040

Fig. 2 - Change in the color of yerba mate leaves during processing (1) Green leaves, (2) after drying, (3) after grinding, (4) after storage. L *) luminosity, a *) hue from red to green and b *) hue from yellow to blue, according to the CIELAB scale. Values in the graph represented with standard deviation.

However, diffusion process is slow and limited. For greater humidity diffusivity to occur, higher temperature gradient between the external environment and the product is necessary (Wray and Ramaswamy 2015). However, submitting yerba mate to very high temperature can shorten the drying time, but can result in excessive degradation. In turn, lower temperature can prevent degradation, but exposes the material to a highly oxygenated environment, which can also cause degradation (Holowaty et al. 2018). Thus, not only temperature, but the time of heat treatment may be responsible for the degradation of chemical compounds, suggesting that adjustments in this binomial (time and temperature) need to be implemented.

Regarding losses of total phenolic compounds and flavonoids (58.8% and 26.3%, respectively), it has been reported that the drying processes also cause degradation of these compounds in medicinal plants and herbs such as *Camelia sinensis, Panax quinquefolium* and *Syzygium samarangense* (Nguyen and Chuyen 2020). Śledź et al. (2013) found significant degradation of phenolic compounds after drying *Origanum vulgare* and *Mentha* sp. and *Ocimum basilicum* (56%, 40% and 34%, respectively) when compared to fresh leaves.

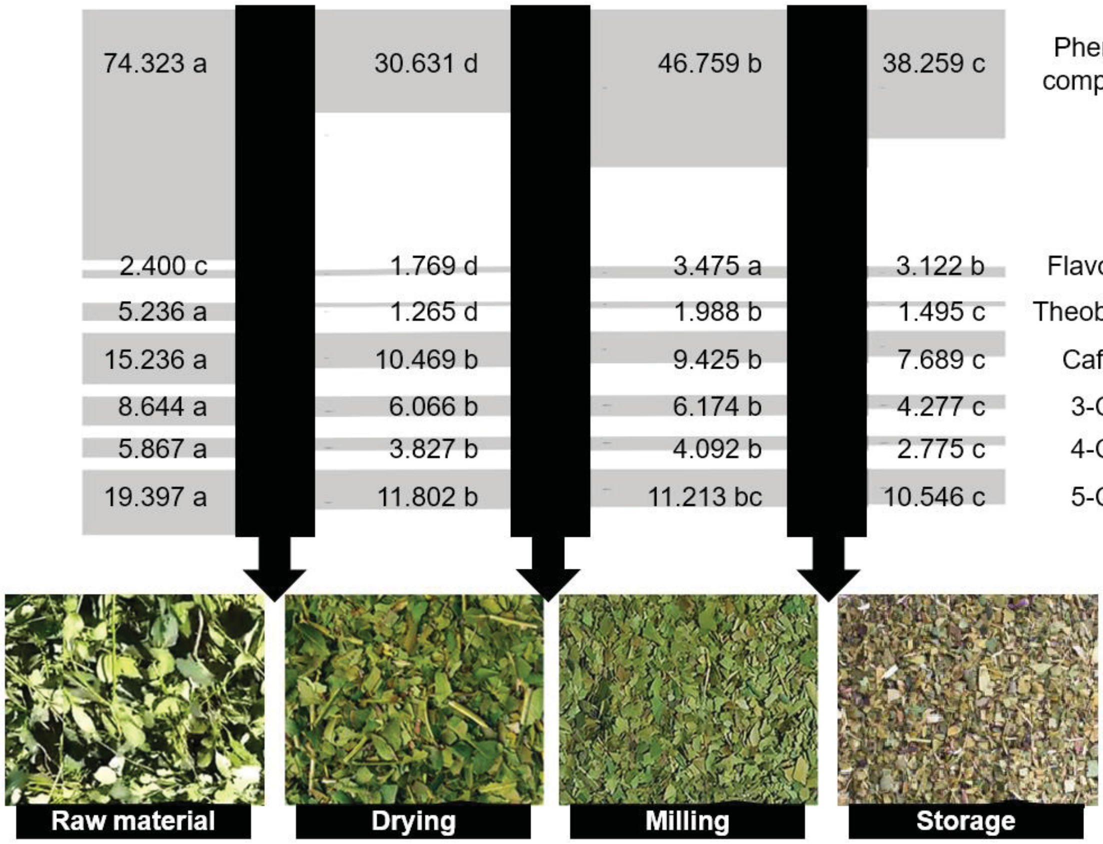


Fig. 3 - Sankey Driagram of the contents of methylxanthines and phenolic compounds in the production process of yerba mate. Values in the graph refer to the average observed with the Tukey's test (different letters indicate significant differences in the line / along the processing).

Other studies confirm the levels of phenolic compounds observed. Mateos et al. (2018), found contents of total polyphenols ranging from 76.5 to 84.9 mg GAE.g^{-1} in *I. paraguariensis* samples. Gómez-Juaristi et al. (2018) found average value of 3.3 mg g^{-1} and Correa et al. (2017) of 5.61 mg g^{-1} for the content of total flavonoids. Other authors also reported 79.1 to 95.9 mg g^{-1} of phenolic compounds in green leaves and, 49.2 to 51.8 mg g^{-1} in yerba mate processed for "chimarrão" (Meinhart et al. 2010; Berté et al. 2014).

Methylxanthines are important contributors to the taste of yerba mate and are related to its stimulating properties (Oestreich-Janzen 2016). The degradation of caffeine in the drying operation reached 31.3%, relatively less than that of theobromine (75.8%). This can be explained by the relatively stable nature of caffeine, as it is known to be very resistant to degradation under different drying conditions (Kulapichitr et al. 2019).

In addition, considering the metabolic route of methylxanthines, theobromine is a precursor to caffeine and that, depending on the case, there may be interconversion between them (Oestreich-Janzen 2016). Thus, in the fresh material, there is a sum of methylxanthines of 20,472, in the drying operation of 11.734, in the grinding operation of 11.413 and in the storage of 9.184, which shows the degradation of these compounds in drying and storage processes; however, in the grinding process, there is only conversion of caffeine into theobromine.

The reported levels of methylxanthines were close to previous studies that indicated that the contents in yerba mate can vary from 7.1 to 32.3 mg g^{-1} for caffeine and from 2.5 to 6.96 mg g^{-1} for theobromine (Konieczynski et al. 2017; Croge et al. 2021).

Hydroxycinnamic acids are often esterified with quinic acid, generically called chlorogenic acids, and specifically known as 3 - CQA, 4 - CQA and 5 - CQA (Verma and Shukla. 2015; Naveed et al. 2018), which also suffered degradation in the drying process of 29.8, 34.8 and 39.2%, respectively.

In order to avoid losses of chemical compounds during heat treatment, other methods can be considered and studied regarding their economic viability for thickly ground yerba mate. For bleaching, there are techniques such as the addition of salts (metal ions), ascorbic acid and citric acid and use of water vapor, already used for some types of teas. Dong et al. (2012) reported that treatment with 0.05% zinc sulfate provided the maintenance of green color in *Eucommia ulmoides* and that functional constituents were maintained after the combination with citric acid before heat treatment.

For drying, other times and temperatures can also be used, as already mentioned. Nguyen et al. (2020) studied four drying temperatures for *Hibiscus* *sabdaria* L. and found that drying at 80º C was the one that best preserved the phenolic compounds and antioxidant activity of this tea. Other methods can also be considered with a focus on creating a less oxidative environment during operation, such as radiation and freeze drying (Dong et al. 2011; Chua et al. 2019). The use of microwaves to dry yerba mate has been previously tested and the authors report that the process was efficient, but did not contribute to greater conservation of color, sugars and caffeine; however, the other compounds have not been evaluated (Passardi et al. 2006).

After drying, grinding was performed, which favored an increase in the content of phenolic compounds, mainly flavonoids. Methylxanthines and chlorogenic acids were stable in this unit operation. Grinding consists of the fragmentation of yerba mate into smaller particles. This change in particle size can make some compounds more available due to the increase in the contact surface (Zaiter et al. 2016). In addition, in this operation, coarse particles, especially branches, are separated, making the leaf / branch ratio higher, which also justifies the changes in the physicochemical properties.

Storage is an operation where yerba mate is stored before being marketed, protected from light and humidity and, generally, at room temperature. This unit operation also aims at maturing and standardizing the sensory characteristics of yerba mate to serve some international markets. Thus, ground yerba mate may or may not be stored. Oxidation reactions that occur during storage change the color and flavor of the product, giving it new attributes (Fig. 2 and Fig. 3). It was observed that there is a new degradation of compounds, with only 5-CQA remaining stable. Greater losses were observed for 3-CQA and 4-CQA with 30.7 and 32.2%, respectively. The lowest degradation was observed for flavonoids, only 10.2% in this operation.

The loss of methylxanthines in this operation also reduces the bitterness of yerba mate, making it smoother, and this is a characteristic appreciated in some markets. However, there are markets where the energy value of yerba mate is highly appreciated and, in this case, storage should not be performed.

Negrão-Murakami et al. (2017) also observed degradation of chlorogenic acids in yerba mate stored for 90 days at temperature of 25ºC. Król et al. (2020) observed average decrease of 83% in the content of total polyphenols and 91.5% in phenolic acids after 12 months of storage of coffee grown under different production systems. Thus, to avoid losses of chemical compounds of yerba mate during storage, other methods need to be studied such as the use of lower temperatures in the storage environment or even alternative packaging to prevent contact with oxygen.

Changes in the chemical composition during processing to obtain thickly ground yerba mate led to changes in the antioxidant capacity evaluated by the ABTS radical capture method (Fig. 4). Green leaves showed the highest antioxidant capacity (94.9% in 7 minutes), followed by unit operations of grinding (45.9%), drying (40.4%) and storage (28.3%). The complete processing reduced the antioxidant capacity of yerba mate by at least 50%, with emphasis on the storage operation for the loss of this property, which was 70% less when compared to the fresh material.

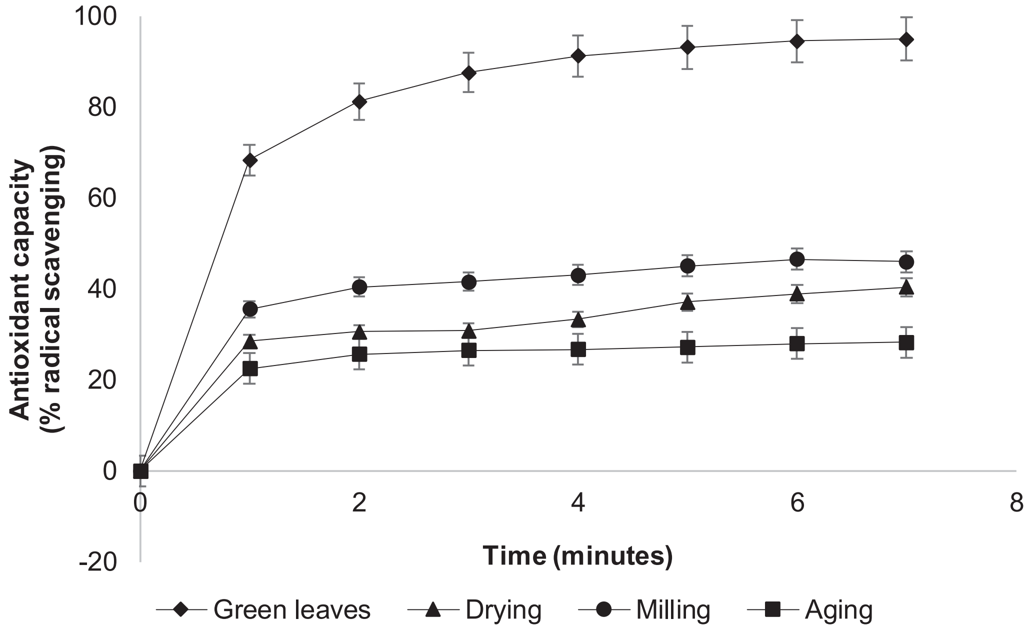


Fig. 4 - Antioxidant activity during the processing of thickly ground yerba mate by the ABTS radical capture method. Values in the graph are the mean plus deviations and evaluated by the time series method.

Fig. 5 shows the correlations between yerba mate compounds and their antioxidant activity throughout the processing. Correlations were different according to the unit operation. In the case of fresh material, strong negative correlations were observed between caffeine and theobromine, which in this case indicates the interconversion between them. In addition, there is also strong negative correlation between 3-CQA and caffeine in this operation.

At the time of heat treatment, new correlations were formed. Strong negative correlation between 5-CQA and phenols, flavonoids and antioxidant activity was observed, which reveals that in this unit operation, there was little influence of this chlorogenic acid on the antioxidant potential of yerba mate. Compounds that most influenced antioxidant activity were 4-CQA and flavonoids.

The correlation between the content of total phenolic compounds and the antioxidant activity in this stage was slightly lower than that observed in other processes. This is associated with the fact that heat treatment degrades these compounds, so that the antioxidant activity tends to decrease, but high temperatures allow the formation of new phenolic compounds from Maillard reactions, which in turn, do not offset or replenish the previous antioxidant potential (Damodaran and Parkin 2017; Bisogin et al. 2019; Bilge 2020).

In other unit operations, grinding and storage, strong positive correlations were generally found, due to the fact that they had similar effects on most compounds.

4.4 CONCLUSIONS

Changes in physicochemical parameters were observed during processing to obtain thickly ground yerba mate. The heat treatment operation, which included bleaching and drying, proved to be highly oxidative and contributed to the greater degradation of the green color and chemical compounds. Compounds with the greatest decreases in this operation were phenolic compounds and theobromine. The storage operation also provided degradation in compounds with higher losses for 3-CQA and 4-CQA. Thus, the development of new technological operations for the preservation of the chemical compounds of yerba mate is a strategy that must be considered. Storage is only indicated to serve markets that require more yellowish color pattern. New correlations for the chemical compounds of yerba mate were presented according to the unit operation.

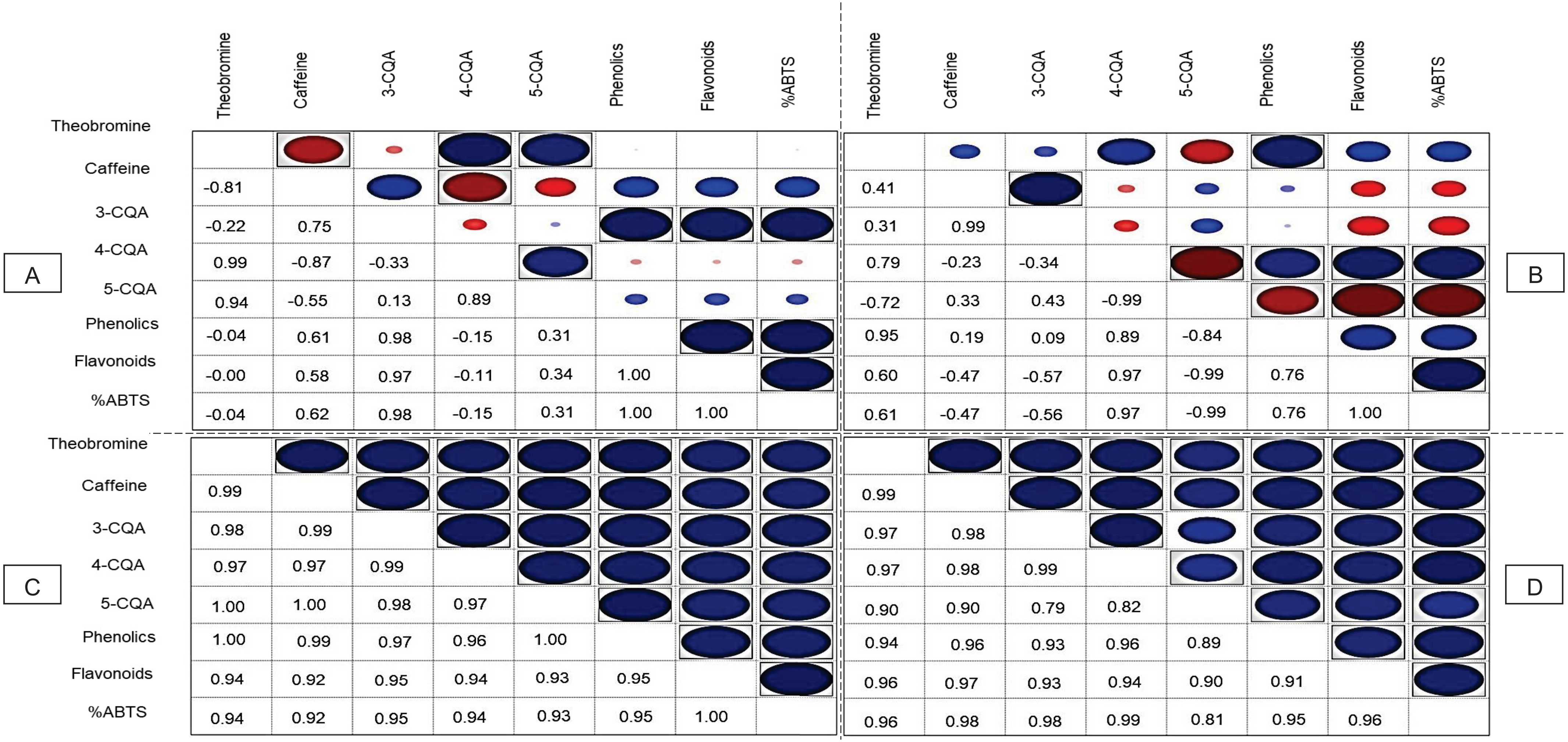


Fig. 5 - Correlogram between chemical compounds and antioxidant activity (% ABTS) according to processing for the production of thickly ground yerba mate. A) Raw material; B) Heat treatment (bleaching and drying); C) Grinding; D) Storage for 120 days. Strong correlations are represented by more intense colors. Blue color represents positive correlation. Red color represents negative correlation. Values represent Pearson's linear coefficient for these correlations. Boxes around circles indicate significant correlations.

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5 INFLUENCE OF THE YERBA MATE PRODUCTION AND PROCESSING SYSTEM ON ITS CHEMICAL COMPOSITION AND SENSORY PROFILE

Article formatted for the Journal of Sensory Studies

Abstract

Several factors such as production, processing and consumption forms can affect the sensory quality of drinks made with yerba mate; however, few studies have been carried out in this regard. The aims of this study were to evaluate the sensory profile of yerba mate produced under different production systems and grinding sizes and to quantify the antioxidant activity, chemical compounds and their correlation with sensory attributes with a focus on indicating the best market destination for elaborated products. In addition, we sought to understand the difference in the flavor profile of the drink when consumed in the form of *chimarrão* and in the form of infusion (thermal cups). The different production and processing systems generate products with different sensory characteristics due to changes in their chemical composition. The container used for consuming the infusion affects the perception of taste by consumers.

Practical Applications

To highlight the *Ilex paraguariensis* species due to its versatile chemical composition and possibility of multiple uses (energy drinks, nutraceutical additives to bioactive cosmetics). To quantify the sensory profile of yerba mate infusion. To relate the sensory quality of yerba mate infusion with its chemical composition and the characteristics of the production process (cultivation and processing). To know which chemical factors affect yerba mate appearance, aroma and taste. To know the influence of grinding and blending with raw materials from different sources in their sensory quality. To know how consumption form affects the perception of taste by consumers.

Key Words: *Ilex paraguariensis* St. Hil.; quantitative descriptive analysis; methylxanthines; phenolic compounds; *chimarrão.*

5.1 INTRODUCTION

In response to the growing demand for healthy products with therapeutic functions, the search for new flavors and differentiated teas has been a trend in the market. In this context, drinks based on yerba mate (*Ilex paraguariensis* St. Hil.), which are already widely appreciated in the American continent, are gaining worldwide market due to their stimulating and therapeutic properties. In addition, yerba mate has stood out due to its quality, price and potential for multiple uses in the food, nutraceutical and cosmetic industries (Godoy et al., 2020; Croge et al., 2021).

Produced mainly by Argentina, Brazil and Paraguay, yerba mate is exported on a large scale to Uruguay and Chile, and to a lesser extent to Europe, the United States, Syria and Japan. In 2017, producing countries harvested more than 1 million tons of leaves from crops in systems ranging from full sun to intercropped with native forests, the so-called shade conditions (Marques et al., 2014; FAO, 2017; Croge et al., 2021).

Although several studies have demonstrated its health benefits, few have been carried out in relation to the quality of drinks made with yerba mate, mainly in relation to its sensory properties (Godoy et al., 2020). Santa Cruz et al. (2002) and Godoy et al. (2020) were the first works related to the definition of sensory descriptors for specific yerba mate products. However, the understanding of how sensory quality is perceived by consumers and which chemical compounds are decisive in this aspect still remains deficient. This information is critical when it is intended to differentiate and / or characterize a product for successful insertion in the global market (Pagliosa et al., 2008; Croge et al., 2018).

Factors such as genetic variety, geographical areas of cultivation, climatic conditions, processing methods, drying speed and temperature, grinding size and infusion methods, participate in the creation of the different sensory properties found in yerba mate products (Bhumiratana et al. 2011; DiDonfrancesco et al., 2014; Croge et al., 2018).

Among the processing stages of yerba mate, blending is a process often carried out by industries for standardization, as products from shaded systems are more valued than those from full sun systems, since shading gives rise to “softer flavor”, which presents better acceptance in the market. In contrast, full sun systems are generally the most productive. Thus, blending between raw materials seems to be a way to combine productivity and quality. However, studies that corroborate the interference of blending or the origin of the raw material in determining yerba mate appearance, aroma and flavor have not been found and this “softer flavor” has not yet been quantified (Valerga et al., 2013; Croge et al., 2018; Croge et al., 2021).

Yerba mate infusion is commonly prepared by placing the product obtained from this processing in contact with water at approximately 70 ° C in specific containers called *cuia*. *Cuias* can be made of various materials such as glass, stainless steel, ceramics, but the most popular is the made with *Lagenaria siceraria* plant. This is the traditional mate or *chimarrão*, which has been part of South American customs for centuries, being one of the symbols of its culture, history and economy. However, yerba mate can go far beyond this traditional use and the implementation of new forms of consumption is a strategy that many industries have been searching for (Croge et al., 2021).

Understanding how the different aspects of yerba mate consumption can affect the perception of consumers of the drink is very relevant, not only from the theoretical point of view, but also from the perspective of practical application. Marketing strategies can benefit from this understanding by implementing its consumption. In addition, the form the drink is consumed can make it more attractive, contributing to improving the taste experience (Holowaty et al., 2018; Bavasso 2019; Croge et al., 2021).

Aims of this study were to evaluate the sensory profile of yerba mate produced under different production systems and grinding sizes and to quantify the antioxidant activity, chemical compounds and their correlation with sensory attributes with focus on determining the best market destination for elaborated products. In addition, we sought to understand the difference in the flavor profile of the drink when consumed in the form of *chimarrão* and in the form of infusion (thermal cups).

5.2 MATERIAL AND METHODS

5.2.1 Yerba Mate samples

Material evaluated in this research came from four commercial yerba mate brands composed of thin leaves and branches and manufactured as specified in Table 1. After preparation, 5 kg of each product to be evaluated were sampled, 3 kg for sensory analysis and 2 kg for analysis of chemical compounds. Total samples were: 3 blend herbs and fine grinding, 3 blend herbs and medium grinding, 2 shade herbs and fine grinding and 2 shade herbs and medium grinding. Each yerba mate sample was evaluated in 3 different production lots, totaling 30 samples. Fine grinding consisted of particles smaller than 1.5 mm, and medium grinding, particles equal to or greater than 1.5 mm. Blending was carried out with the mixture of leaves and fine branches harvested from full sun and shade crops as detailed in Table 1.

TABLE 1 – Characteristics of products evaluated in this research.

Name	**Composition**	Grinding (1)
Yerba mate 1	60% leaves and branches in full sun + 40% shade (blend)	Fine
Yerba mate 2	65% leaves and branches in full sun + 35% shade (blend)	Fine
Yerba mate 3	70% leaves and branches in full sun + 30% shade (blend)	Fine
Yerba mate 4	60% leaves and branches in full sun + 40 % shade	Medium
Yerba mate 5	65% leaves and branches in full sun + 35% shade (blend)	Medium
Yerba mate 6	70% leaves and branches in full sun + 30% shade (blend)	Medium
Yerba mate 7 Yerba mate 8	100 % leaves and branches in shade	Fine
Yerba mate 9 Yerba mate 10	100 % leaves and branches in shade	Medium

(1) In fine grinding, particles were smaller than 1.5 mm and in the medium grinding, particles were larger than or equal to 1.5 mm.

5.2.2 Panelists

Yerba mate sensory evaluation team was composed of 12 trained judges of both sexes aged 18-56 years. Schooling varied from high school to graduate studies and the frequency of yerba mate consumption was greater than or equal to 3 times a week. The team was trained specifically for this work in yerba mate sensory attributes and quantitative descriptive analysis.

5.2.3 Sensorial evaluation procedure

Work of the team of judges began with the 'focus group' qualitative method described by Della Lucia & Minin (2013). With this method, it was possible to establish, based on the most used descriptive terms for infusions, the characters or descriptors most appropriate to the yerba mate sensory profile (Figure 1). In the training stages, descriptors were defined and difference, triangular and ordering tests for color scales and for the recognition and standardization of aromas and flavors were applied as described in Table 2 (Chaves & Sproesser, 2013). Training sessions were carried out over 6 months.

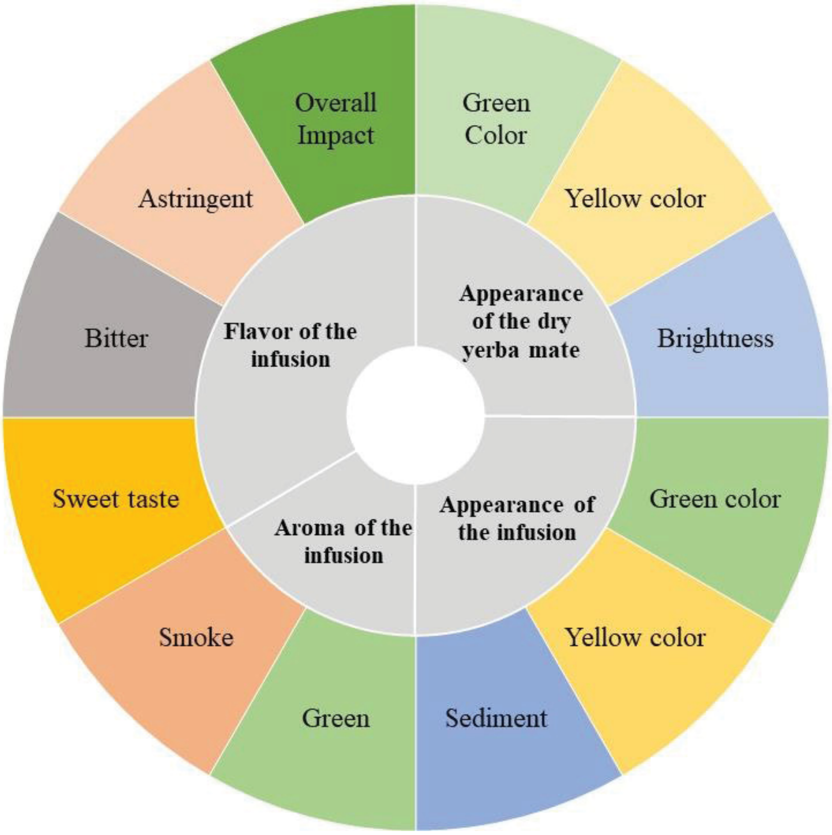

Figura 1 – Descritores dos atributos sensoriais da erva-mate determinados pelo método ‘grupo de foco’ com 12 julgadores treinados. Metodologia descrita por Della Lucia & Minin (2013).

Sensory profile mapping was performed by the quantitative descriptive analysis method (QDA), which used a 15 cm unstructured scale, anchored beyond the extremes with terms that indicated the intensity of the attribute to be evaluated by trained judges, according to methodologies by Chaves & Sproesser (2013) and Monteiro et al. (2017).

Yerba mate samples were encoded with random three-digit numbers generated by the R software. Each evaluation session lasted 90 minutes. Five samples were served, per session, in random order. To clean the palate, trained judges received water, unsalted cookies and peanuts (Chaves & Sproesser, 2013).

Dry yerba mate appearance was evaluated with the product placed in transparent glasses, to which, subsequently, water was added for the evaluation of the infusion appearance by trained judges. The concentration used in this stage was 0.125 g mL^{-1}.

Yerba mate infusion submitted to aroma and flavor evaluation was prepared with water at 70 ± 2 ° C at concentration of 0.125 g mL-1, according to manufacturers' recommendations. After 2 minutes, the infusion was filtrated and transferred to 200 ml non-transparent sealed thermal cups. Trained judges were not allowed to remove the seal, but only to assess aroma and taste through a small opening.

The last stage carried out by the team of judges consisted of a new flavor evaluation; however, using the traditional method of yerba mate consumption. For this, 1 portion of each yerba mate was used. The infusion was served in containers called *cuias*, made of glass, with the insertion of the stainless steel pump for the suction of the infusion. In each container, 62.5 g of yerba mate were added with adjustment of the container so that the product occupied one side of the *cuia*, according to recipe for the preparation of *chimarrão* (Meinhart et al., 2010). On the opposite side, 200 mL of water at 70 ± 2 ° C were slowly added. Containers were covered with aluminum foil so that there was no interference of appearance in the evaluation and, after 2 minutes, the infusion was offered to judges.

5.2.4 Analysis of chemical composition

To determine bioactive compounds, 0.5 kg of each sample was dried in microwave, operating at 2450 MHz, until reaching constant weight and, later, samples were ground in processor (Frizon et al., 2015). For analysis, samples were submitted to extraction process with water at 70ºC and 70% methanol, according to methodology of Heck et al., (2008) and Gullón et al. (2018). All tests were performed in triplicate.

Total content of phenolic compounds was determined from the Folin-Ciocalteu solution, with spectrophotometric reading at wavelength of 725 nm and results expressed in mg of gallic acid equivalent (GAE) (Riachi et al., 2018). The content of total flavonoids was also quantified by the spectrophotometric method and results were expressed in mg of quercetin equivalent (QE) (Buriol et al., 2009).

TABLE 2 - Definition of descriptive terms for yerba mate for quantitative descriptive analysis (QDA) performed by 12 trained judges.

Attributes	Definitions	Reference
Green / yellow coloring of dry herb	Color intensity.	Green: fresh yerba mate. Yellow: standard Uruguay yerba mate stored for at least 1 year.
Brightness	Color vividness.	Fresh yerba mate.
Color Green / yellow color infusion	Intensity of green or yellow color in water.	Infusion of fresh yerba mate and aged yerba mate.
Sedimentation	Amount of particles that settle to the bottom of the glass.	Measuring the size of the block formed at the bottom of the glass with a ruler.
Herbaceous aroma	Characteristic aroma of fresh yerba mate.	Yerba mate and Camelia sinensis
Smoke aroma	Aroma from the firewood combustion process.	Camelia sinensis and smoked yerba mate.
Sweetness	Sweet taste, smooth.	Yerba mate with 0.5% sucrose
Bitterness	Bitter taste ranging from weak to strong.	Yerba mate infusions ranging from 0.5 to 3%.
Herbaceous flavor	Characteristic flavor of yerba mate, relative to the natural product.	Infusions of stored and fresh yerba mate.
Astringency or residual taste	Sensation that remains in the mouth for a few seconds after swallowing the drink.	Green banana and Yerba Mate infusions ranging from 0.5 to 3%

To quantify the antioxidant activity, the kinetic reaction between antioxidants present in the sample and the ABTS free radical was used, according to methodology of Jeszka-Skowron et al. (2016). The ABTS free radical scavenging activity was estimated by the following equation: % radical scavenging = ((Abs control - Abs sample) / (Abs control)) x 100, where Abs is the absorbance.

The quantification of methylxanthines (caffeine and theobromine) and monocaffeoylquinic acids (3 - caffeoylquinic acid (CQA3), 4 - caffeoylquinic acid (CQA4), 5 - caffeoylquinic acid (CQA5)) was performed by HPLC as described by Lima et al. (2016) and Tolessa et al. (2016). For detection, wavelengths of 280 nm were used for caffeine and theobromine and, 320 nm, for CQA3, CQA4 and CQA5. Results were expressed in mg per g of sample (mg g^{-1}).

5.2.5 Data analysis

This research was approved by the Committee for Ethics in Research involving Human Beings of the State University of Maringá (COPEP / UEM) and registered under CAAE number 67545317.0.0000.0104.

Data from the sensory evaluation in thermal cups and chemical compounds were submitted to principal component analysis (PCA) with the FactoMineR package of the R software. For comparison of the flavor profile in *cuia* and thermal cups, analysis of variance was performed (ANOVA) followed by the Tukey test. Results were graphically expressed with average followed by coefficient of variation.

5.3 RESULTS AND DISCUSSION

Yerba mate was presented as a product with differentiated sensory profile (Figure 2). In the appearance attribute, green color stood out with the highest scores on the scale. Herbaceous aroma stood out when compared to the smoke aroma. Regarding flavor, there seems to be a balance between bitterness, astringency and sweetness, with slightly lower scores for sweet taste. The overall impact ranged from 8.5 to 12.4, indicating that yerba mate has impact on the palate from strong to very strong. The results obtained also demonstrated that the different yerba mate production and processing systems yielded products with different sensory characteristics.

Sensory characteristics of yerba mate, in turn, are defined by its chemical composition (Figure 3). In the multivariate principal components analysis (PCA), very specific clusters were formed in terms of composition and particle size, with samples distributed in all PCA quadrants. It was observed the existence of two principal components with eigenvalues > 1, responsible for 87.9% of the total variance in the data set, with Factor 1 (Dim 1) representing 58.8% and Factor 2 (Dim 2) 29.1%.

Factor 1 (Dim 1) is positively related to green color, luminosity and herbaceous aroma and Factor 2 (Dim 2) to smoke aroma, CQA4 and CQA3. Both factors are also positively

related to bitter taste, overall impact, caffeine, theobromine and sedimentation. Yellow color, sweet taste and CQA5 attributes are strongly and negatively related to

Factor 1. In contrast, weak relationship between these factors and astringency, antioxidant activity (ABTS) and phenolic compounds was observed (Figure 3).

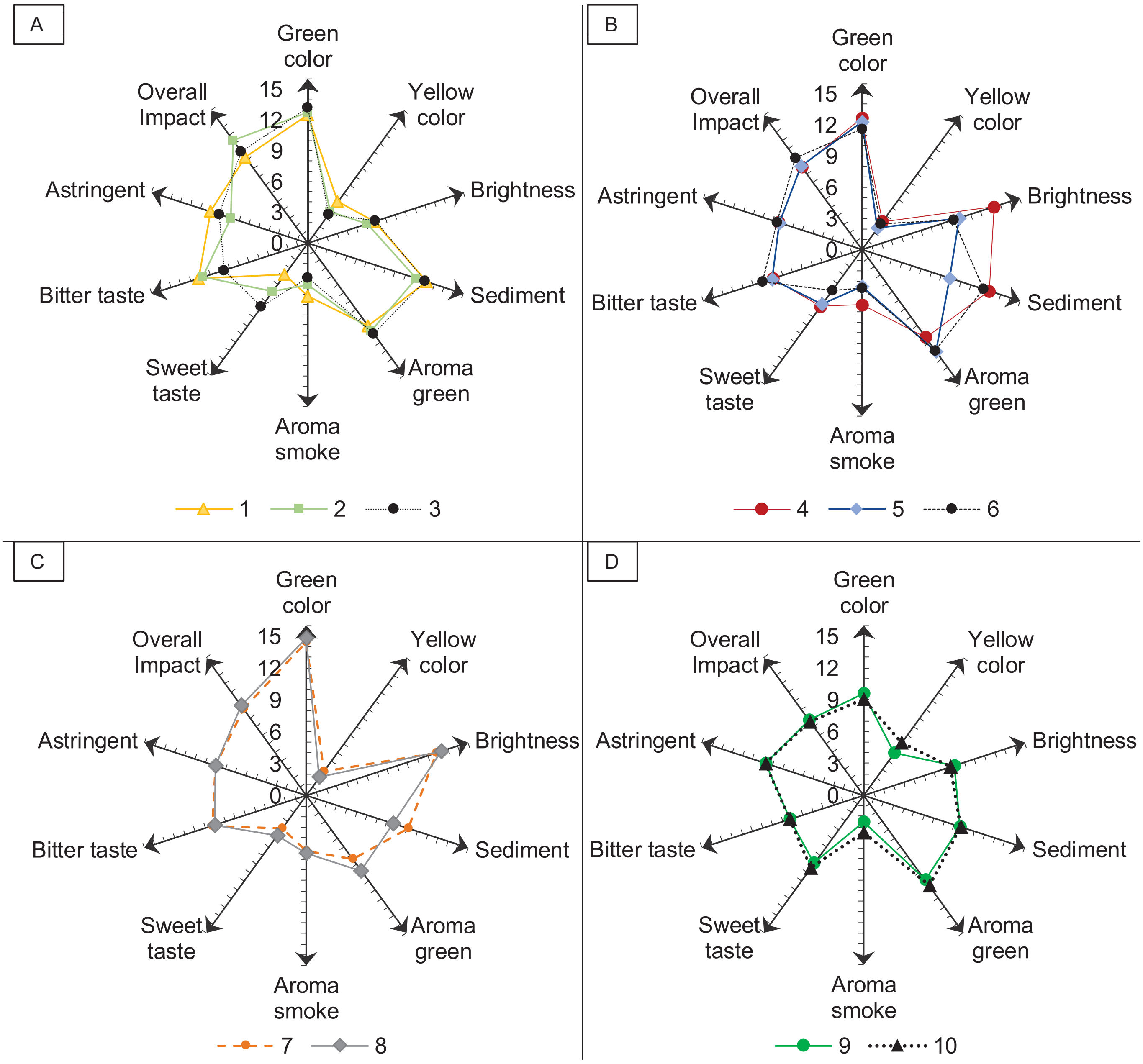

Figure 2 - Sensory profile of different types of yerba mate according to the production system (blend or shade) and grinding size (medium or fine). Each value is represented by the average obtained in the quantitative descriptive evaluation, with a 15-point scale performed by 12 trained judges. A: blend / fine grinding; B: blend / medium grinding; C: shade / fine grinding; D: shade / medium grinding.

High correlation between green color, luminosity and herbaceous aroma attributes was observed (Figure 3). Yerba mate color is one of the most notable and important characteristics to indicate the quality of the product. Each market requires a color characteristic; the Brazilian market is highlighted by the preference for bright green color, while consumers in Argentina, Paraguay, Uruguay and Chile prefer opaquer color, such as olive green and yellow tones (Zaions et al., 2014; Holowaty et al., 2016; Holowaty et al., 2018). Thus, to serve the Brazilian market, herbs from the shade system and fine grinding stand out (7 and 8), while yellow tones were found in those from shade system and medium grinding (9 and 10) (Figures 2 and 3).

In this sense, shade system and fine grinding seem to favor the green color and luminosity of samples (Figure 3). Several studies suggest that shade leaves are usually greener and brighter, as they have higher chlorophyll concentration per area unit for maintaining the energy balance in the plant and increasing the absorption of red light, which is limited in shady environments of forests and agroforests (Boeger et al., 2009; Lopes & Lima, 2015). High intensities of solar radiation in plants maintained in full sun system can lead to luminous saturation, reducing the green color of leaves (Caron et al., 2014).

In addition, the higher luminosity provided by fine grinding is due to the smaller particles coming from this technology, which provide greater reflection of light. De Oliveira-Mendes (2005) observed that yerba mate fractions showed ever more intense greens as particle size decreased.

High correlation was also observed between bitterness, overall impact and content of methylxanthines (Figure 3). It is known that flavor is a mixed experience of taste, smell, tactile and visual sensations (Spence, 2020). In this sense, overall impact was defined as the maximum sensory sensation during the tasting time (Sanchez & Chamber, 2015). Thus, greater correlation of this sensation was observed with bitterness attribute, which means that bitter taste was more significant for this determination.

The bitterness formation is related to production and processing factors that directly influence the content of chemical compounds of yerba mate as shown in Figure 3. Bitterness is an important attribute of several foods consumed worldwide including cocoa, coffee, green tea, black tea and, of course, yerba mate, which is also appreciated and classified for its bitter taste (Pagliosa et al., 2009; Chaves & Sproesser, 2013).

In some regions, bitterness is responsible for the differentiation of yerba mate into strong or soft. This distinction creates preferences among consumers. In this way, it is observed that most blend herbs are located in the first PCA quadrant together with vectors of bitter taste, overall impact, caffeine and theobromine. In other words, regardless of grinding, blend herbs were those with the greatest bitterness and overall impact and methylxanthines were the main substances responsible for these attributes (Figures 2 and 3). Shade herbs with medium grinding were those with lower methylxanthines, bitterness and overall impact values.

Theobromine contents varied between 1.298 and 3.096 mg g^{-1} and caffeine contents varied between 4.977 and 12.902 mg g^{-1} (Table 3). Mateos et al. (2018) observed caffeine content of 8.83 ± 0.27 mg g^{-1} and theobromine content of 1.16 ± 0.04 mg g^{-1} in samples of commercial yerba mate brands, values close to average values obtained in this work.

Furthermore, the average relationship between methylxanthines observed was 8.388 mg g^{-1} of caffeine for 2.266 mg g^{-1} of theobromine, which classifies yerba mate as a moderate source of these compounds (Table 3). Therefore, it can be used as an alternative to coffee and in formulations for the production of energy drinks. Correia et al. (2018) reported that the amount of caffeine contained in 100 ml of yerba mate infusion corresponds to the same amount contained in 10 ml of espresso, 118 ml of cola extract or 0.5 g of powdered guarana.

Tolessa et al. (2016) reported that shading conditions affect the quality of coffee and found variations in caffeine content analyzing the interaction between shading and altitude. Ji et al. (2018) compared the influence of shade on the production of compounds in green tea leaves at the same physiological age and observed increased caffeine and theobromine levels in leaves grown for 10 days in full sun, compared to leaves grown with 100% shading.

In vegetables, methylxanthines are involved in nitrogen and carbon metabolism, and environmental conditions capable of limiting photosynthesis, such as shading, can provide lower levels. In addition, these substances absorb UV radiation in their aromatic core and, therefore, higher radiation levels can favor their production to reduce stress conditions for the plant. Developmental stage, seasonal and management changes also influence the levels of methylxanthines (Tolessa et al., 2016; Ji et al., 2018). Thus, in order to obtain higher caffeine and theobromine levels for yerba mate products, blend composed of raw materials from full sun and shade systems is indicated.

Another flavor attribute defined as important is astringency, residual taste or aftertaste that remains in the mouth after swallowing the drink. It is a sensorially desirable property, except when at very high levels (DiDonfrancesco et al., 2014; Sanchez & Chamber, 2015). In this study, strong correlation between astringency and the presence of phenolic compounds was observed due to the proximity of their vectors in the PCA (Figure 3). These compounds have high affinity for saliva proteins and, from this interaction, the formation of precipitates occurs, which promote astringent sensation in the mouth (Damodaran & Parkin et al., 2017).

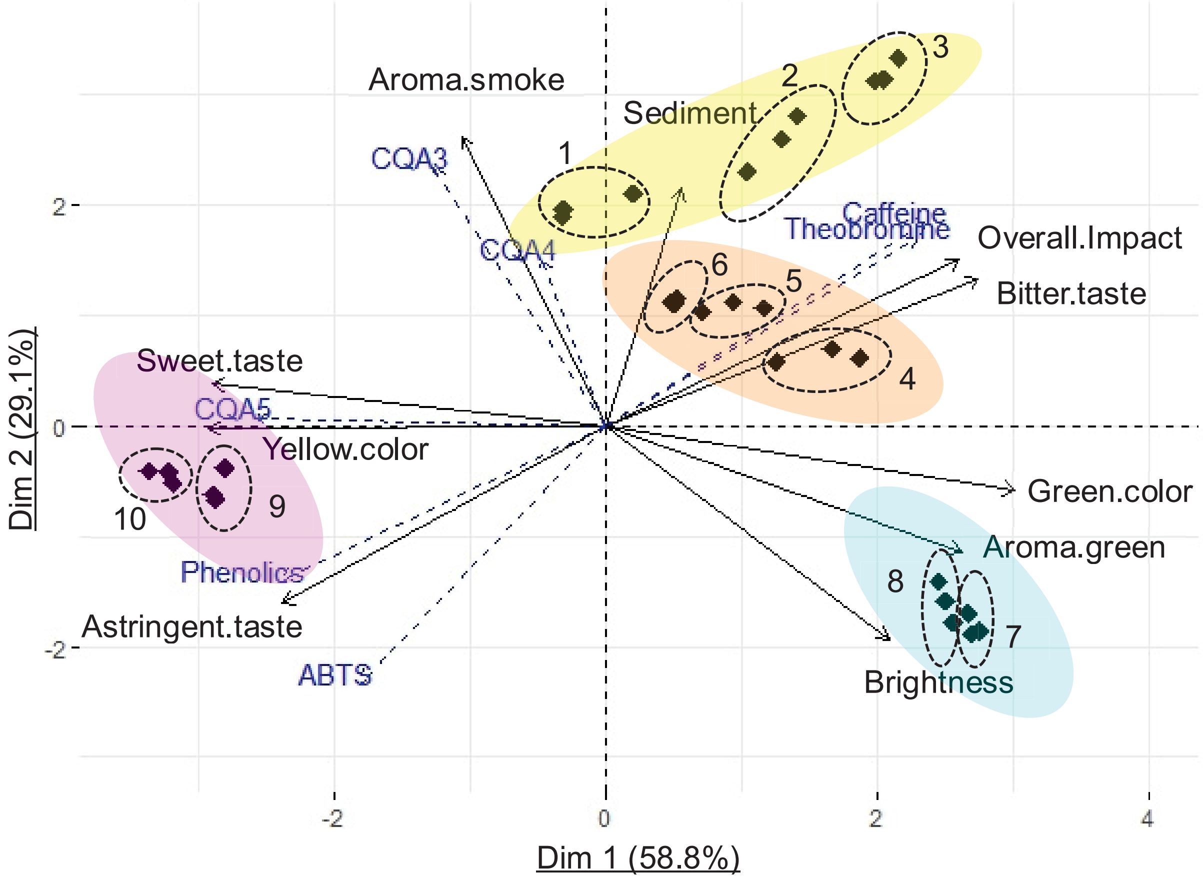

Figure 3 - Description of the sensory attributes and chemical composition of yerba mate of different patterns analyzed by principal components analysis (PCA). Sensory analysis was performed by the quantitative descriptive method with 12 trained judges. Distribution of the different yerba mate patterns (Blend / fine grinding 🟨; Blend / medium grinding 🟥; Shade / medium grinding 🟪; Shade / fine grinding 🟦.

Medium grinding and shade yerba mate were defined with greater astringency, high antioxidant activity by the ABTS method, presence of phenolic compounds, CQA5, sweet flavor and yellow color (Figure 3). In other words, the origin of shade and medium grinding seemed to provide smooth flavor, with tendency of samples to be sweeter or smoother, less bitter and more astringent (Figure 2).

Balance of flavor between bitter and astringent was observed for shade and fine grinding yerba mate, since shade with fine grinding favored the oxidation of phenolic compounds, thus reducing astringency, which is explained by the quadrants occupied by each one of them (Figure 3). For cocoa-based products, for example, the use of grinding to improve flavor is common, since lower astringency is observed when extracts are ground into smaller particle sizes (Anderson et al., 2018).

The highest production of total phenolic compounds was observed in shade samples with medium grinding and the lowest production was observed for blend samples with fine grinding (Table 4). Thus, when the market requires products with higher antioxidant levels and concentration of phenolic compounds, shade yerba mate with medium grinding is indicated.

In this study, the average values observed for phenolic compounds was 35,483 mg GAE g^{-1} with values ranging from 30,632 to 44,312 (Table 4). Meinhart et al. (2010) found similar average values for 5 different types of yerba mate: 47.8 mg per g. Gullón et al. (2018), in turn, found significantly higher average values in yerba mate industrial waste after 30 minutes of extraction (55.82 mg GAE g^{-1}).

Regarding grinding, Cordoba et al. (2019) found higher concentration of total polyphenols in coffee with coarser grinding when compared to that with finer grinding. The authors also concluded that grinding is one of the factors for the preparation of drink with the greatest impact on physicochemical parameters. Other studies have established that particle size and distribution are parameters that affect and determine the diffusion of solids during the infusion process, thereby inducing changes in color and chemical composition (Cordoba et al., 2019a; Cordoba et al., 2019b).

Frizon et al. (2015) also found higher concentration of phenolic compounds in shade areas (cultivation intercropped with eucalyptus) compared to area under full sun. Chemically, the main enzyme involved in the synthesis of these compounds is phenylalanine ammonium lyase (PAL). Action of this enzyme is regulated by environmental factors such as temperature and water availability. In addition, the intensity and quality of light is also crucial to regulating its metabolic synthesis. In general, the high temperatures found in full sun systems favor the oxidation of these compounds (Louie et al., 2006; Verma & Shukla, 2015; Taiz et al., 2017; Fukuda, 2019).

Table 3 - Methylxanthines (theobromine and caffeine) in yerba mate infusions of different patterns. Mean followed by standard deviation.

		Theobromine (mg g^{-1})	Caffeine (mg g^{-1})
Blend/fina	1	2.348 ± 0.180	10.460 ± 0.153
	2	3.096 ± 0.053	12.771 ± 0.131
	3	2.920 ± 0.071	12.112 ± 0.341
Blend/média	4	2.218 ± 0.163	8.810 ± 0.088
	5	2.556 ± 0.005	9.497 ± 0.031
	6	2.267 ± 0,040	10.565 ± 0.004
Sombreada/fina	7	2.494 ± 0.065	9.358 ± 0.044
	8	1.879 ± 0.022	7.789 ± 0.057
Sombreada/media	9	1.298 ± 0.013	4.992 ± 0.240
	10	1.508 ± 0.013	4.977 ± 0.132
Median		2.266	8.388
CV (%)		14.140	16.830

Média seguida do desvio padrão.

Considering the antioxidant activity evaluated by the ABTS free radical scavenging activity, higher values were observed for shade yerba mate with medium grinding, followed by shade yerba mate with fine grinding, that is, the shading system seems to be associated with greater antioxidant potentials, reaching values greater than 70% of free radical scavenging activity (Table 4).

Gullon et al. (2018) also reported high *in vitro* free radical scavenging percentages in yerba mate samples, with values ranging from 75 to 93.7%. Anesini et al. (2012) compared the antioxidant activity of yerba mate with another standard synthetic antioxidant (ascorbic acid) and found maximum values for both close to 75%. Konieczynski et al. (2017) compared the antioxidant activity of yerba mate, green tea, black tea and oolong tea and found greater antioxidant capacity for yerba mate samples.

Lower antioxidant activity was observed for blend yerba mate with fine grinding compared to others, highlighting that the more intense the grinding, the greater the degradation of antioxidant compounds. Hu et al., (2012) also observed decrease in free radical scavenging activity as the size of tea particles decreased. In addition, compounds that most influenced the antioxidant capacity of yerba mate were total phenolics, which underwent oxidation when submitted to more intense grinding (Figure 3).

Table 4 - Phenolic compounds and antioxidant activity in yerba mate infusion of different patterns.

		Phenolic compounds (mg g^{-1})	Antioxidant activity (% ABTS)
Blend/fine	1	32.931 ± 0.070	56.890 ± 0.271
	2	30.632 ± 0.535	55.165 ± 0.283
	3	32.436 ± 0.220	59.421 ± 0.223
Blend/medium	4	33.597 ± 0.222	61.234 ± 0.021
	5	33.981 ± 0.049	62.448 ± 0.119
	6	35.195 ± 0.260	64.357 ± 0.050
Shade/fine	7	35.948 ± 0.048	73.745 ± 0.083
	8	36.106 ± 0.075	77.098 ± 0.412
Shade/medium	9	44.312 ± 0.415	84.153 ± 0.044
	10	39.693 ± 0.469	81.332 ± 0.054
Mean		35.483	67.584
CV (%)		10.622	14.830

Mean followed by standard deviation.

Table 5 - Chlorogenic acids in yerba mate infusion of different patterns. Mean followed by standard deviation.

		3-Cafeoilquinic acid	4-Cafeoilquinic acid	5-Cafeoilquinic acid
Blend/fine	1	7.284 ± 0.276	3.570 ± 0.022	9.823 ± 0.271
	2	5.971 ± 0.236	3.657 ± 0.088	10.713 ± 0.283
	3	6.306 ± 0.260	4.005 ± 0.028	13.330 ± 0.223
Blend/medium	4	5.805 ± 0.102	3.724 ± 0.076	12.186 ± 0.021
	5	6.063 ± 0.003	4.173 ± 0.003	11.326 ± 0.119
	6	6.171 ± 0.003	4.093 ± 0.001	11.240 ± 0.050
Shade/fine	7	5.421 ± 0.048	4.137 ± 0.105	10.952 ± 0.083
	8	4.386 ± 0.096	2.920 ± 0.191	10.529 ± 0.412
Shade/medium	9	5.683 ± 0.043	3.643 ± 0.061	14.421 ± 0.044
	10	5.876 ± 0.099	3.835 ± 0.053	12.475 ± 0.054
Mean		5.889	3.724	11.896
CV (%)		11.896	9.545	11.404

Mean followed by standard deviation.

The chlorogenic acid found in greater amounts and the most relevant in determining the sensory profile of yerba mate was CQA5, and, similar to total phenolic compounds, higher levels were observed in shade samples with medium grinding (Figure 3). Correa et al. (2017) also found, among chlorogenic acids, higher concentration of CQA5, when compared with CQA3 and CQA4. The average levels observed were 11,896 for CQA5, 5,889 for CQA3 and 3,724 for CQA4 (Table 5). These acids were also determinants of the sensory profile of yerba mate and contributed to the quality of the drink.

Butiuk et al. (2016) demonstrated strong influence of production factors in relation to the content of chlorogenic acids. In this study, high correlation between CQA3, CQA4, smoke aroma and sedimentation was observed (Figure 3). In addition, smoke aroma and sweet flavor occupied the same quadrant in the analysis, revealing association among these attributes. Smoke aroma is specifically related to the process used by the industry, in which drying is performed by burning wood. Many compounds have already been identified in smoke and, among them, some phenolic acids stand out. Another compound primarily associated with smoke aroma is guaiacol. Heo et al. (2020) reported high association between guaiacol, smoke aroma and sweet taste in coffee samples.

High correlation between CQA5, sweet taste and yellow color was also observed. Some studies suggest that the sweet taste found in teas is due to the presence of compounds such as galactose, fructose, glucose and sucrose (Damodaran & Parkin, 2017). Dartora et al. (2011) identified fructose, glucose and sucrose in different yerba mate samples. Godoy et al. (2020) also found sweet taste as an important sensory attribute for toasted yerba mate tea and in the multivariate analysis, it was positioned in the opposite quadrant of the bitter taste, similar to results obtained in the present study.

Drinking is a behavior determined by a complex combination of physiological, perceptual, cultural and social variables. Different sensory aspects are decisive for the final perception of a given food or drink. In particular, some studies have shown that the perception of taste can be affected by the type of container in which the drink is served and / or consumed (DiDonfrancesco et al., 2014). Thus, regarding the flavor profile of the yerba mate infusion, results reveal that the form of consumption, as well as the container used to consume it, provided changes in the intensities of the analyzed attributes (Figure 4).

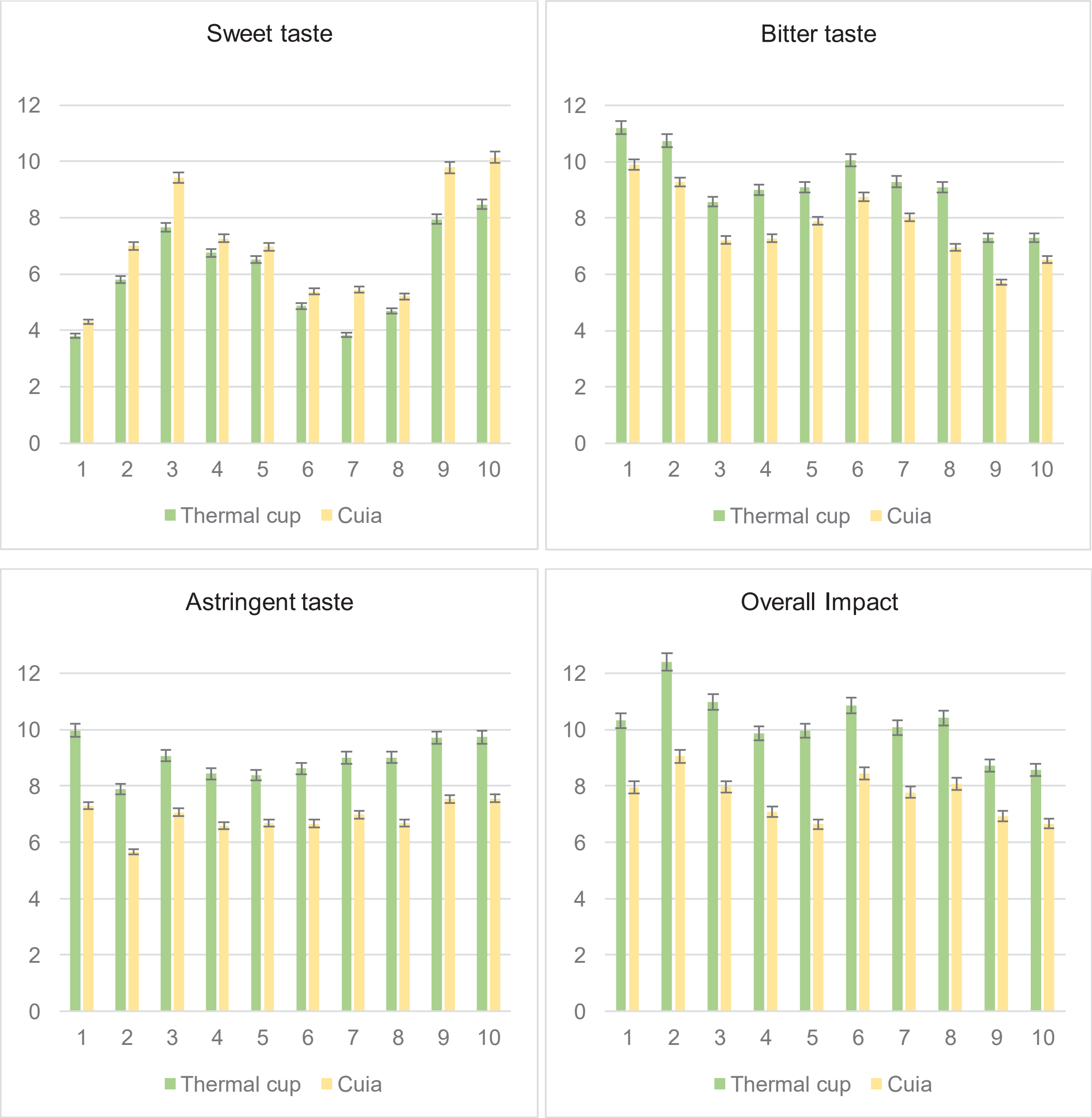

Figure 4 - Flavor profile by the quantitative descriptive analysis method of 10 yerba mate samples evaluated in thermal cups and in *cuias*. Average values are presented with standard deviation.

The perception of sweetness increased when the infusion was offered in *cuias*. The perception of all other flavor attributes (bitterness, astringency and overall impact) decreased when judges consumed the product in *cuias*, a traditional way of drinking *chimarrão*. Thus, it has been shown that the traditional act of consuming *chimarrão* contributes to the softening of the sensory characteristics of the drink (Figure 4). This information can help consumers who prefer softer drink with lower overall impact to consume yerba mate in this traditional way. Those who prefer drinks with more pronounced intense flavor, tending to bitter and astringent, should consume yerba mate in the form of infusions similar to tea and coffee.

5.4 CONCLUSION

Production and processing systems generate products with different sensory characteristics. These sensory characteristics are correlated with the chemical composition of the product.

Higher phenolic compound, antioxidant activity and astringency levels were observed in shade herbs. However, the more intense the grinding, the greater oxidation of these compounds. Thus, when the purpose is to obtain products with higher antioxidant levels and concentration of phenolic compounds, shade yerba mate with medium grinding is indicated.

Higher methylxanthine, bitterness and overall impact levels were observed in blend herbs. Thus, when the market requires products with stimulating properties, with higher theobromine and caffeine levels, blend yerba mate is indicated.

Shade production system and fine grinding are strongly associated with luminosity and green color attributes. When aiming for greater flavor balance, this herb seems to be the most suitable, as it has balance between bitterness and astringency.

Container used for the consumption of yerba mate infusions affects the perception of taste by consumers. The traditional *chimarrão* contributes to the softening of the drink's sensory characteristics.

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6 CONCLUDING REMARKS

This work shows multiple potential uses of yerba mate due to its chemical and sensory quality. It also confirms the species as promising in relation to production, as the activity can be very profitable for farmers and entrepreneurs. It also shows the need for innovation in the sector with the use of high technology both in the production of raw material and in its agro-industrial processing.

Cultivation systems and their characteristics, as well as the harvesting seasons, changed the agronomic performance of yerba mate. The open forest production system stood out for combining quality and productivity. It is also noteworthy that this system provides environmental benefits with the maintenance of the landscape and forest remnants. Marketing strategies can benefit from this, developing products that meet consumer demand, associating health promotion with environmental preservation. In this context, the open forest system, for being exploited mostly in forest fragments with Araucaria, can contribute to the preservation of some native species, in particular, *Araucaria angustifolia* (Bertol.) Kuntze, currently at risk of extinction.

Another possibility that the open forest system provides is organic cultivation, which is increasingly valued in the market for guaranteeing to the end consumer the mitigation of the risk of contamination by possible pesticide residues, combined with preservation of the environment and responsible use of natural resources.

Processing operations bring changes in the physicochemical composition of yerba mate. Many losses occur in the process as a whole, reducing the levels of energy and antioxidant compounds. The knowledge of the effect of unit operations on the content of each compound gives a direction to the industry in the sense of the need to better conduct this process without affecting the quality of the final product.

In addition, it was evident that the flavor of yerba mate is different and that blends and grinding size generate products with different sensory characteristics. If the market requires more intense and bitter products, strong in relation to their energy content, the use of blends is recommended, that is, a mixture between raw materials from shade and full sun systems. This can strengthen the production chain, since different production systems can be used. Alternatively, the use of raw materials from 100% shade systems is indicated to obtain products rich in phenolic compounds and which stand out due to their high antioxidant capacity.

6.1 RECOMMENDATIONS FOR FUTURE WORKS

The current knowledge about yerba mate requires the conduction of further studies. Studies in the agronomic area should be carried out to obtain quality raw material through breeding programs, selection of varieties and production and management strategies in efficient systems. Researches associated with rural extension that favor the revaluation and improvement of the management of yerba-mate systems in forest remnants as a way of promoting and increasing income in rural areas and conservation of natural resources (forests, soil and water).

Studies aimed at implementing new uses, such as preservatives, food supplements, dyes or hygiene products and cosmetics, should be carried out so that consumption becomes increasingly broad and accessible.

Studies aimed at the development of industrial technological operations to optimize the biological activity of yerba mate should also be carried out, in association with studies on the sensory acceptance by consumers.

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Address: Rua Tibiriçá, 1094, sala 101, Centro CEP: 14010-090

Ribeirão Preto – SP

Pedro Cardoso Santos - POLI TRADUÇÕES
Office: 55 16 3201-8170
Mobile: 55 16 99606 0616

contato@politraducoes.com.br

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CNPJ: 02.584.240/0001-06

Endereço: Rua Tibiriçá, 1094, sala 101, Centro - CEP: 14010-090

Ribeirão Preto – SP

Prof. Pedro Cardoso Santos - POLI TRADUÇÕES
Mobile: 55 16 99606 0616

contato@politraducoes.com.br

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CNPJ: 02.584.240/0001-06

Endereço: Rua Tibiriçá, 1094, sala 101, Centro - CEP: 14010-090

Ribeirão Preto – SP

Prof. Pedro Cardoso Santos - POLI TRADUÇÕES
Mobile: 55 16 99606 0616 (WhatsApp)

contato@politraducoes.com.br

www.politraducoes.com.br