Short Communication

Phytochemical composition of extracts from yerba mate *chimarrão*

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Abstract
Yerba mate is a tree natural from South America, traditionally daily consumed as hot (*chimarrão*) or cold (*tereré*) and roasted leaves (mate tea) infusions, being an important source of polyphenols and flavonoids in human nutrition. To produce bioactive-rich extracts from yerba mate, oven-dried leaves at 35 °C and three different commercial products, named M, T, and S, were extracted using different General Recognized as Safe solvents (distilled water (W), ethanol (E), and water: ethanol (1:1, v:v) (WE)). The yerba mate extracts were analyzed for total and soluble solids, titratable acidity, total phenolic content (TPC), total flavonoid content (TFC), and antioxidant activity. The WE solvent resulted in the highest TPC and TFC. However, the commercial samples showed a higher concentration of phytochemicals than oven-dried leaves, and the commercial sample T showed the lowest content of total solids and the highest content of soluble solids (°Brix). The industrial processing of yerba mate aids the TPC and TFC preservation, resulting in extracts with superior phytochemicals concentration when compared with the oven-dried sample.

Keywords Antioxidant activity · Flavonoids · *Ilex paraguariensis* · Maté beverages · Phenolic compounds

1 Introduction

Yerba mate or maté (*Ilex paraguariensis* A.St.-Hil.) is a native tree from South America and it has a natural distribution area of 540,000 km^2 between northwest Argentina, eastern Paraguay, and southern Brazil [2]. In these regions, it has great environmental and socio-economic importance, creating jobs and increasing incomes, as it is the main non-timber forest product [22]. The parts of the plant used are the leaves and variable fractions of thin branches. Traditional consumption is carried out by locals as a hot infusion (*chimarrão*), cold infusion (*tereré*), or even as hot or cold roasted leaves infusions (mate tea). Many consumers drink 1–2 L/day of yerba mate infusions, which correspond to about 12–23 g/habitants/day [4, 7]. This amount is equivalent to the consumption of tea (*Camellia sinensis*) in Asia and Europe, and coffee in Europe and North America [4].

The yerba mate bioactive compounds with functional properties (about 10% in dry weight) are particularly polyphenols, chlorogenic acids (caffeoylquinic (CQA), and dicaffeoylquinic acids (DQA)) and caffeic acid; alkaloids, caffeine, and theophylline; flavonoids quercetin, rutin, lutein, and myricetin; and terpenoids ursolic and oleanolic acids [2, 16, 17]. These phytochemicals are known for their anti-inflammatory, anti-obesogenic, antimutagenic, antibacterial, and antiviral capacity, as well as their antioxidant capacity [1, 3, 4, 8, 9, 12, 20].

The main steps for *chimarrão* and *tereré* mate industrial processing are the *sapeco* (thermal bleaching using flames), flash drying at high temperatures (300–400°C), milling, sieving, and particle size standardization [13, 18]. The mate phytochemical extraction and purification also have high technical and economic potential. However, the extraction procedure and solvent type impact

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the phytochemicals recovery, being preferred General Recognized as Safe (GRAS) and environmentally friendly solvents.

We hypothesize that industrial processing decreases the concentration of the phytochemical compounds in fluid yerba mate extracts. For this reason, the aim was to produce bioactive-rich extracts from oven-dried leaves and different commercial *chimarrão*-type yerba mate with different GRAS solvents.

2 Material and methods

Between March and May 2017, *in natura* leaves of yerba mate were collected from Laranjeiras do Sul, Paraná State, Brazil (25° 24′ 28" S 52° 24′ 57" O). The samples were from 10-year-old trees, agroforestry shaded, with random and stratified sampling in all parts of the plant. All leaves were oven-dried at 35ºC for 72 h, followed by knife milling (Fortinox, Star FT-50, Brazil). Three commercial yerba mate brands (M, T, and S) of native leaves for *chimarrão* (no added sugar), manufactured in March and April of 2017, non-vacuum packed, were purchased from groceries of the same city. Each sample was sieved at 20 *mesh* to remove small and thin branches and stems and vacuum stored at -20 °C.

All samples were extracted (8 g in 40 mL of solvent) by distilled water (W), anhydrous ethanol (E), and water: ethanol 1:1 (v:v) (WE), after 5 h of water bath Dubnoff incubation (50 °C) [14]. The extracts were evaluated for soluble and total solids, and total titratable acidity [23]. The total phenolic content (TPC) was analyzed using Folin Ciocalteu reagent, and the results were express as gallic acid (G7384, Sigma-Aldrich San Luis, Missouri, EUA) equivalent (GAE) [5]. The total flavonoid (TFC) content was investigated by aluminum-flavonoid complexation, and the results were express as catechin (C1251, Sigma-Aldrich San Luis, Missouri, EUA) equivalent [10]. Total antioxidant capacity was determined by the scavenging of free radicals DPPH (2,2-Diphenyl-1-picrylhydrazyl, D9132, Sigma-Aldrich San Luis, Missouri, EUA), and ABTS (2,2′-Azino-bis (3-ethylbenzothiazoline-6-sulfonic acid), A1888, Sigma-Aldrich San Luis, Missouri, EUA), and the results were express as Trolox® ((±)-6-Hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid, 238,813, Sigma-Aldrich San Luis, Missouri, EUA) equivalent. All results were expressed in dry mass of yerba mate and statistically evaluated by analysis of variance and Duncan's test mean comparison ($p > 0.05$) (SAS® Institute Inc, Cary, USA).

3 Results and discussion

The different solvents influenced the total solids of the fluid extracts (Table 1). Ethanol provided the highest of extracted total solids, followed by WE ($p < 0.05$). The concentration of total solids can reflect the yield of the extraction process, being influenced by the solubility of solids in solvents, sample particle size, and the separation or filtration of the solid particles. Therefore, smaller particles tend to favor extractive processes, as they have a big contact surface area, and also make it difficult to remove them by filtration processes, resulting in high total solids concentrations [1].

Commercial products resulted in the highest soluble solids ($p < 0.05$), mainly for water extraction (Table 1). The quantification of soluble solids is an easy and fast tool to estimate the content of sugar, organic acids, and small constituents in food products [21]. The use of ethanol, even if diluted (1:1), favors the extraction of sugar, organic

Table 1 Total solids, soluble solids, and titratable acidity of yerba mate extracts

	Solvent	Yerba Mate			
		F	M	S	T
Total solids (g 100 g^{-1})*	W	a 1.97 ± 0.97 B	a 1.04 ± 0.28 B	a 1.82 ± 0.17 A	a 1.20 ± 0.28 A
	E	a 4.55 ± 0.26 A	b 2.82 ± 0.55 A	c 1.68 ± 0.09 A	c 0.90 ± 0.16 A
	WE	ab 1.92 ± 0.17 B	a 2.46 ± 0.15 A	bc 1.32 ± 0.54 A	c 0.93 ± 0.15 A
Soluble solids (°Brix)*	W	c 1.29 ± 0.19 C	a 3.47 ± 0.38 B	b 2.02 ± 0.14 C	a 3.42 ± 0.21 C
	E	ab 45.57 ± 2.06 A	b 43.71 ± 0.54 A	ab 45.30 ± 0.61 A	a 46.47 ± 0.31 A
	WE	c 41.12 ± 0.07 B	b 44.47 ± 0.35 A	b 44.02 ± 0.21 B	a 45.40 ± 0.09 B
Titratable acidity (g citric acid 100 g^{-1})*	W	ab 0.14 ± 0.06 A	a 0.19 ± 0.03 A	ab 0.14 ± 0.01 A	b 0.09 ± 0.01 A
	E	b 0.04 ± 0.00 B	b 0.03 ± 0.01 B	a 0.08 ± 0.01 B	b 0.03 ± 0.01 C
	WE	a 0.15 ± 0.03 A	a 0.16 ± 0.03 A	b 0.04 ± 0.00 C	b 0.05 ± 0.01 B

*Means of three determinations plus/minus standard deviation. Means followed by different uppercase letters (in same column) indicate differences between solvents and lowercase (in same line) indicate differences between yerba mate samples by Duncan's test ($p < 0.05$). F: Oven-dried leaves. M: Commercial brand mate 1. S: Commercial brand mate 2. T: Commercial brand mate 3. W: water solvent. E: ethanol solvent. WE: water:ethanol solvent (1:1. v:v)

acids, and other components, with a polarity similar to that of the solvent, present in yerba mate samples. The lowest acidity was observed in the ethanol extracts, except for the commercial sample S, showing that extraction of acids was hampered using ethanol (Table 1).

The TPC extraction using WE was more efficient than the solvents W and E, especially in the commercial yerba mate (Table 1). Only in the oven-dried sample (F), the solvent did not experience effects in the polyphenols extraction ($p > 0.05$) (Table 1). Regarding the type of yerba mate, it was observed that the content of phenolic compounds was related to the yerba mate processing (Table 2). The highest TPC was observed in commercial yerba mate band M (65.78 ± 1.54 mg gallic acid g^{-1}) using WE solvent. Sample F resulted in the lowest TPC extraction, using WE as the solvent. The oven-dried sample was not bleached, and enzymes could continue active during mild temperature oven-drying and milling steps. The temperature that was used (35 °C) was not enough to inactivate the polyphenol oxidase and peroxidase enzymes which naturally occur in yerba mate leaves [7, 18], resulting in products with lower phytochemical compounds.

Phenolic compounds feature a variety of chemical structures, ranging from simple molecules to high degree polymerized molecules [19]. Based on this, the differences in the concentration of total phenolic compounds in the aqueous, alcoholic, and hydroalcoholic extracts (Table 2) were consistent, since hydroalcoholic solvents are considered more useful in the extraction of this class of compounds.

The leaves, branches, and bark from *I. paraguariensis* have different phenolic compound classes and concentrations [20]. Total phenolic compounds and antioxidant activity, by DPPH scavenging, were high in methanolic and aqueous extracts from bark and branches than from leaves samples [20]. Commercial products did not inform in the labels which concentration of the tree part (leaves and branches) composed the product consequently, showing a natural variation of color, flavor, and phytochemical composition. Besides, during the milling process, larger branches can be re-milled to the standardization of commercial products. Therefore, the sample F, composed exclusively of leaves, should consequently present higher antioxidant activity. However, this sample showed the highest antioxidant activity (Table 2). This result corroborates TPC and TFC, suggesting that enzymatic degradation promoted greater influence than thermal degradation at yerba mate compounds. It results in products with relatively low antioxidant activity and, ethanolic extracts tended to show higher antioxidant activity than water extracts.

The WE extracts showed high total flavonoids concentration, except for the F yerba mate sample ($p < 0.05$) (Table 2). The highest flavonoid content was observed in commercial T (5357 ± 373 mg catechin g^{-1}) using WE solvent. It has been reported high flavonoids content using WE compared to W when analyzing extracts from yerba mate residues [11]. The results can be due to the high rutin extracting [13], and low quercetin solubility in water [6]. Both groups, phenolic and flavonoids compounds, have

Table 2 Total phenolic and total flavonoids compounds, and antioxidant activity of yerba mate extracts

	Solvent	Yerba Mate			
		F	M	S	T
Total phenolic compounds (TPC)*	W	ab 57.89 ± 1.12 A	ab 57.19 ± 1.70 B	b 55.23 ± 1.41 B	a 58.98 ± 0.10 B
	E	a 58.71 + 0.82 A	b 54.48 ± 1.19 B	a 57.41 ± 1.02 AB	a 58.16 ± 1.17 B
	WE	c 59.41 ± 0.48 A	a 65.78 ± 1.54 A	c 58.88 ± 1.05 A	b 61.85 ± 1.53 A
Total flavonoids compounds (TFC)*	W	c 1055 ± 306 C	bc 1433 ± 229 C	b 1643 ± 39 C	a 2537 ± 102 C
	E	a 3625 ± 131 A	b 3106 ± 93 B	ab 3471 ± 209 B	ab 3293 ± 94 B
	WE	c 2625 ± 54 B	b 4323 ± 247 A	b 4498 ± 48 A	a 5283 ± 372 A
DPPH*	W	ab 23,572 ± 398 A	a 23,803 ± 99 A	c 22,326 ± 38 A	b 23,036 ± 20 A
	E	a 23,107 ± 179 A	a 21,521 ± 1194 AB	a 21,219 ± 142 B	a 23,059 ± 1218 A
	WE	a 23,374 ± 186 A	a 22,724 ± 112 B	c 19,806 ± 570 C	b 21,044 ± 33 A
ABTS*	W	ab 336 ± 7 A	c 297 ± 13 A	bc 308 ± 10 A	a 353 ± 18 A
	E	c 275 ± 19 B	ab 323 ± 28 A	b 313 ± 9 A	a 352 ± 9 A
	WE	a 270 ± 11 B	c 176 ± 7 B	b 199 ± 1 B	bc 182 ± 13 B

*Means of three determinations plus/minus standard deviation. Means followed by different uppercase letters (in same column) indicate differences between solvents and lowercase (in same line) indicate differences between yerba mate samples by Duncan's test ($p < 0.05$). F: Oven-dried leaves. M: Commercial brand mate 1. S: Commercial brand mate 2. T: Commercial brand mate 3. W: water solvent. E: ethanol solvent. WE: water:ethanol solvent (1:1. v:v). TPC expressed in mg GAE g^{-1}, TFC expressed in mg catechin g^{-1}, DPPH expressed in μM Trolox® g^{-1}, ABTS expressed in μM Trolox® g^{-1}

structures that are characterized by their high antioxidant potential [3].

Thereby, the yerba mate extracts stand out because of their high antioxidant capacity compared to other plants and tea herbs [16]; and the ethanolic extracts tend to show higher antioxidant activity than water extracts. The WE solvent (1:1, v:v) resulted in extracts with a higher concentration of total phenolic compounds and flavonoids than W or E, which correlate with antioxidant activity [15].

4 Conclusion

The GRAS solvent WE resulted in mate extracts with high total phenolic and flavonoid compounds, which corroborate with antioxidant activity. Oven-dried leaves, non-thermal bleached, showed the lowest phytochemical compound concentration on fluid extracts. The commercial yerba mate T presented the lowest content of total solids and the highest content of soluble solids (°Brix) among all brands, indicating good extraction efficiency of WE solvent. Oppositely to our initial hypothesis, the industrial yerba mate processing for commercial products resulted in superior yield extraction and preserves the phenolic and flavonoids compounds, compared to the mild drying process of mate leaves. The WE solvent and commercial yerba mate samples can be used for extract production, being safe and useful for drugs or food production and manufacturing.

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Data Availability The supporting data are available from the corresponding author upon reasonable request.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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