Conformity assessment of product quality in the consumer market

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Abstract. Among the traditional types of tea in the Russian market, Chinese Pu-erh tea has a special place. In the work, samples of Pu-erh tea presented on the market of Voronezh were investigated. The samples of black and green tea were compared. By mass fraction of moisture, water-soluble extractive substances, total ash, and the share of soluble ash, all tea samples met the standards. The amount of tannin in some samples of Pu-erh tea was low — 4.6–6.0% in NE; in terms of antioxidant activity (AOA), AOA, they were also inferior to black and green tea. A general positive correlation of tannin and AOA levels was noted. The fact that not all polyphenols have antioxidant properties is evidenced by the fact that the tannin content in tea samples differed by 7 times, AOA - by 3 times. To determine the antioxidant activity (AOA), we used the electrochemical titration method on an Expert-006 instrument in a cell with a background electrolyte — KBr in a H₂SO₄ solution; the marker is ascorbic acid. It is established that the method is simple, convenient; gives a relative error within 5%.

1. Introduction

Tea is one of the most common drinks in the world. The tea market is very diverse. This has always been due to the taste characteristics of tea leaf drinks. In addition to the known types of tea, depending on the technology of processing the tea leaf - white, green, black, etc., new varieties are offered to the consumer; a variety of blends of tea with other plant materials [1-3]. Currently, many studies have established important properties of tea for human health [4-6]. In China, Thailand, Japan, and other countries, some types of tea are positioned as functional or used in traditional medicine [7–9]. Mainly, in this regard, much attention is paid to the study of the chemical composition of tea extracts [10]. The beneficial properties of tea are associated with antioxidant, antimicrobial activity due to various phenolic compounds [11, 12]. Thanks to the development of instrumental methods of analysis — gas and liquid chromatography, mass spectrometry, IR spectroscopy, and others — carbohydrates, cyclic alcohols, glycosides, organic acids, colorants, and aromatic compounds are identified in tea extracts [8, 13-16]. The conducted studies reveal differences in the composition and properties of tea varieties and types [1, 17, 18], the relationship of composition and health benefits [6, 19], the course of transformation of substances in the process of tea fermentation [9, 20, 21], the influence of technological processes on the spectrum of compounds in tea [22], extraction conditions for the complete extraction of useful substances and increase their bioavailability [23-28].
Chinese Pu-erh tea is known for its features in the origin of raw materials, cooking technology and useful properties [1, 29, 30]. According to the definition of the state Chinese standard GB / T 22111-2008, Pu-erh is this tea, produced according to a unique technology from the leaves of tea trees growing in the territory of Yunnan. Depending on the production technology, Pu-erh is divided into two main types: shen and shu. Shen Pu-erh technology involves fixing the tea leaf, drying and autoclaving. Shu Pu-erh is made by a special method of "wet storage" and deep fermentation. In recent years, Pu-erh tea has been popularized in Russia; the promotion of a new type of product on the market includes diversified activities, including the use of classification methods in forecasting consumer demand [31]. Product quality in the model building chain is of paramount importance [32]. Pu-erh tea is sold not only in tea and specialized stores, but also in large retail chains. However, there is not enough objective information about this tea; and Russian consumers are often faced with falsification.

The present work is devoted to the study of physicochemical quality indicators, the level of tannin and antioxidant activity (AOA) of Pu-erh tea samples in comparison with black and green tea samples presented on the consumer market of Voronezh.

2. Materials and methods

Three samples of Pu-erh, sold at the supermarket, were chosen as objects of study — pu-mandarin powder (No. 1), pressed Pu-erh with orange (No. 2), and green pressed Pu-erh in the form of Xiao Tocha (No. 3) — produced under the brand name “Tea Factor”, Saint Petersburg; three samples of tea sold in a specialty store – Shu Pu-erh “Jumbo Dragon”, China; tea factory Yiu Jinglong Lao Shu (No. 4), Shu-Pu-erh “Jinlung”, China; Yunnan Xianguan Tuo-cha Tea (Group) Co (No. 5); Shu Pu-erh “Xiaaguan”, China; Meng Hai tea factory (No. 6); black tea “Azerchay”, Russia, Krasnodar Territory; LLC “Kuban-Ti” (No. 7); Bilochun green tea, China, Beijing, Uuytay Joint-Stock Company (No. 8).

To study tea samples, it was ground in a laboratory mill for 1 min.

The mass fraction of tea moisture was determined by drying a weighed portion of tea (3 ± 0.0002) g in pre-prepared containers at a temperature of (103 ± 2) °C to constant weight (within 6 hours, followed by control after 1 hour).

The total ash content in tea was determined according to ISO 1575: 1987, water-soluble ash - according to ISO 1576-2013.

To determine water-soluble extractive substances, 200 cm³ of hot distilled water was added to a tea sample (2 ± 0.0002) g, boiled under reflux for 1 h, then filtered in a hot condition under vacuum through a glass filter, washed the flask 5 times with hot distilled water (general volume 200 cm³), transferring the entire insoluble precipitate to the filter and then drying the filter cake at 103 °C to constant weight.

To obtain a tea extract, a weighed portion (2.5 ± 0.0002) g was placed in a homogenizer vessel with a capacity of 400 cm³; 250 cm³ of distilled water were brought to a boil and poured onto this sample. Next, homogenization was carried out for 2 min at 12.0 thousand min⁻¹. The extract was filtered through dense non-woven. Such an extract was used to determine tannin, antioxidant activity.

The tannin content in tea was determined by the permanganate method. Exactly 10 cm³ of the extract was placed in a bowl, 750 cm³ of tap water, 25 cm³ of indigo carmine solution were added and titrated with 0.1 M KMnO₄ solution with constant stirring with a glass rod until yellow with a golden hue. The amount of tannin (A),% on dry matter (CB) of tea was determined by the formula

\[ A = \frac{(a-a_1) \times 0.004157 	imes 100}{v_1 \times m} \]

where (a-a1) is the amount of 0.1 M KMnO₄ solution spent on the oxidation of tannin and on the titration of a solution of water and indigo carmine, respectively, cm³; 0.004157 — amount of tannin oxidized by 1 cm³ of a 0.1 M KMnO₄ solution, g; v is the amount of tea extract obtained, cm³; v1 - amount of tea extract taken for testing, cm³; m - weight of a sample of absolutely dry tea, g.
Determination of the antioxidant activity (AOA) of the tea samples studied was carried out using an Expert-006 coulometric titrator. The principle of operation of the device is based on the use of the Faraday law, according to which the mass of the analyte is determined by the amount of electricity spent on the reaction. The analyte is titrated in an electrochemical cell containing a pair of generator electrodes and an indicator electrode used for bipotentiometric determination of the titration end point, an electrolyte for generating a titrating reagent, and an analyte sample. A solution of 0.2 M KBr in a 0.1 M solution of H2SO4 was used as an electrolyte. The device was calibrated with ascorbic acid. Titration conditions: measurement level (potential of the initial and final value of the indicator system) 150 mV; reduction level (the value from which the electrolysis process begins) 40 mV; maximum current strength 50 mA; mixing time 20 s. 1 cm3 of tea extract was introduced into the cell of the device. The display of the device displayed the mass of antioxidants in mg, which was converted to 1 g of CB tea.

All results were statistically processed: for \( n = 2 \) (mass fraction of moisture, ash, extractive substances, tannin) - the repeatability condition is met; at \( n = 5-7 \) (AOA) - using the criteria of Grubbs and Student (\( p = 0.95 \)).

### 3. Results and discussion

The results of determining some of the physicochemical characteristics of tea samples are shown in Table 1. In terms of quality indicators, all tea samples were in compliance with Russian regulatory documents and the Chinese standard GB / T 22111-2008: mass fraction of moisture - not more than 10–13%; the content (%) of water-soluble extractive substances is not less than 28–35; total ash - 7.5–8.5; the proportion of water soluble ash is not less than 45.

| Indicators                             | Sample Number |
|----------------------------------------|---------------|
|                                        | 1 2 3 4 5 6 7 8 |
| Moisture content, %                    | 8.0 7.8 8.7 7.5 7.0 6.9 7.4 7.2 |
| The content of water-soluble extractive substances, % | 30.0 32.2 41.7 28.5 29.6 30.9 27.7 38.3 |
| The total ash content, %               | 6.8 6.1 6.5 7.2 7.2 7.4 8.3 5.7 |
| The proportion of water-soluble ash from the total, % | 45.5 45.0 60.3 46.2 46.9 48.5 46.9 65.7 |

The antioxidant activity of tea can be evaluated by various methods - radical removal, electrochemical with different markers and others [1, 7, 8, 33]. The results of AOA measurement on an Expert-006 instrument for some tea samples are shown in Table 2. The analysis time was within a few minutes. The relative error did not exceed 5%. Thus, the device is very convenient for determining AOA; calibration is provided for other reference samples, in addition to ascorbic acid.

The content of tannin and AOA of tea samples are summarized in table 3. The results of this study showed that the tannin content was very different in the tea samples studied.

Phenolic compounds are important components of tea leaf and infusion from it. As shown by numerous studies, this is a large and diverse group of compounds that are represented by simple derivatives of phenols, flavonoids and polyphenols [17, 18]. The accumulated data provide information on the main differences between black, green, white tea. Based on the chemical composition and mathematical modeling, a classification of unfermented teas has been proposed [18].
Table 2. Measurement results on the Expert-006 instrument

| Measurement number | Sample No. 3 | Sample No. 6 | Sample No. 8 |
|--------------------|--------------|--------------|--------------|
|                    | τ, s mg      | τ, s mg      | τ, s mg      |
| 1                   | 115.80 6.082461 | 55.60 2.882090 | 91.60 4.773678 |
| 2                   | 115.30 6.046122 | 57.20 2.903027 | 91.30 4.747977 |
| 3                   | 115.45 6.059586 | 58.00 2.934164 | 90.10 4.666107 |
| 4                   | 115.00 6.031142 | 58.90 3.001368 | 91.05 4.711483 |
| 5                   | 116.40 6.145556 | 58.15 2.962349 | 89.05 4.648992 |
| 6                   | 115.55 6.069891 | 58.10 2.958285 | 90.80 4.695200 |
| 7                   | 120.10 6.197581 | 60.20 3.516097 | 87.55 4.502337 |

In Pu-erh tea samples, 43 phenolic compounds were identified; analyzed the difference between the number of polyphenols and the degree of maturation [29]. At present, Russian standards do not provide for the control of tea at the level of phenolic compounds. In the standard for tiled black tea, which was valid until 2015, the tannin level was set to a minimum of 8.0%. The Chinese standard sets the recommended polyphenol content for Shen Pu-erh green tea to 28.0%; for fermented tea and shu Pu-erh - 15.0%.

Table 3. Tannin content and antioxidant activity of tea samples

| Indicators                     | Sample Number |
|-------------------------------|---------------|
|                               | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  |
| Tannin,%                      | 5.2 | 5.0 | 35.8 | 6.5 | 6.2 | 9.3 | 12.1 | 24.5 |
| AOA, mg ascorbic acid per 1 g | 277 | 195 | 665 | 228 | 277 | 340 | 433 | 508 |
| E_{OA} for AOA,%              | 3.51 | 2.36 | 1.28 | 2.14 | 3.05 | 3.23 | 2.47 | 2.22 |

Thus, according to the information presented above, in tea samples No. 1, 2, 4, 5, the level of tannin was lower than recommended by the Russian regulatory document. These samples were inferior in tannin content to black and green tea. Perhaps, for tea samples No. 1, 2 this is due to the presence of additives, the properties of raw materials, drying conditions, etc. [13, 21, 22]. Shu Pu-erh (No. 4, 5), have a complex technology, in addition, their properties depend on age.

The very high tannin content of the “green Pu-erh tea” sample suggests that it is made from the top leaves, the manufacturing conditions and shelf life are not violated. Bilochun green tea showed a higher polyphenol content compared to black tea, which is logical and noted in many works, in particular, similar data were obtained in the study of green, black and herbal teas, but the differences in these samples were not so significant [one].

In general, a positive correlation is observed between the content of polyphenols and AOA, but the constituents of the polyphenolic tea complex have unequal AOA [17, 19]. A statistically indistinguishable level of polyphenols of 10% was found in Pu-erh, Fujian and Lyubao tea samples. At the same time, differences were found in AOA measured by various methods: epigallocatechin gallate was responsible for AOA determined by the electrochemical method; for cellular antioxidant activity - common flavonoids [17]. In the study of Pu-erh tea from 15 samples, all showed activity to remove radicals; no direct relationship between the age of tea and AOA has been established [29].

The data obtained in this work show that a positive correlation was observed between the tannin content and antioxidant activity, but the differences in AOA were not so sharp: the maximum and minimum values of tannin content differed 7.1 times, AOA 3.4 times, which confirms the data on the
difference in antioxidant properties of the components of the polyphenolic complex of tea of various types.

4. Conclusion

Studies have shown that the Expert-006 device makes it possible to quickly and reliably determine AOA of tea. Pu-erh tea, presented on the Voronezh market, meets the requirements of the standards for the main quality indicators. As for the beneficial properties of tea, which are associated with the presence of antioxidants, some samples of shen Pu-erh and shu Pu-erh did not have the proper level of tannins and were inferior to the samples of black and green tea in these indicators. Therefore, the provision on the unconditional benefit of Pu-erh tea samples on the market is ambiguous. With a high content of tannin and AOA, a sample of Pu-erh tea had a name that did not correspond to Pu-erh tea (“green Pu-erh tea”), which makes it difficult to identify Pu-erh tea. Thus, monitoring the quality of tea and a professional approach to the classification and characteristics of this product are necessary so as not to mislead the consumer.

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