Classification of Korean Green Tea Products Based on Chemical Components

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ABSTRACT: The prices of domestic green tea products are relatively expensive and price differences within products of the same levels of quality are various. Also, there is no basic criteria on evaluation of green tea quality. To group 43 commercial green tea products into several parts by the principal component and cluster analyses, this work was done by use of 8 chemical constituents which were analyzed by NIR system. The principal component and cluster analyses revealed 8 groups. The first group included 16 products that had lower free amino acid and theanine contents. The second group included 5 products having higher free amino acid and theanine contents, but lower ash contents. The third group included 13 products showing medium values of 8 constituents. The IV group included 4 products having higher contents of moisture, free amino acids, and theanine. The V group included 1 product showing higher moisture but lower catechins contents. The VI group included 2 products that had higher moisture and catechins contents, but lower free amino acid and theanine contents. The VII group had higher moisture and catechins contents. The VIII group had higher ash and vitamin C contents. The free amino acid contents which were the most important in flavor evaluation of green tea quality did highly positively correlate with the contents of total nitrogen (0.956**), theanine (0.981**), and caffeine (0.793**), but negatively with the contents of ash (-0.884**). The catechins used as for functional ingredients did correlate with contents of caffeine (+) and vitamin C (-), respectively.

Keywords: NIR system, principal component, cluster analysis, similar distance, green tea product, chemical component

S eventy percentage of tea consumed worldwide is fermented tea and 22% is non- or semi-fermented tea which is consumed in Korea, Japan, and China Owing to its distinctive savory flavor, green tea is one of the most popular teas in Korea. It is known that the flavor of green tea is affected substantially by the kind of green tea leaves and the processing methods used. Tea quality is recognized as a first-class article as for earlier picking of leaves and younger

leaves in the same time of picking than older leaves (Kim *et al.*, 1997).

As raw-materials from young leaves of tea trees, different types of teas are made with different varieties, production sites, growing seasons, ways of tea manufacturing, shapes, favors, and others. Practically, it is difficult to classify the commercial selling teas exactly, and also evaluation criteria are various. In general, in Korea, manufactured tea products have been classified by fermentation degree, picking time of tea leaves, color of products.

Fresh tea leaves contain moisture of about 75-80%, and solid matter of 20-25%, and soluble components are under 50%. The soluble components contain polyphenols (tannın, catechins), amino acids, caffeine, polysaccharide, and others that are important to flavor. The catechins are attributable to bitter and astringent taste among unique flavors of tea, and also caffeine and saponin have an effect on bitterness. The amino acids are attributable to savory, sweet, and sour flavor. The nucleic acids, sugar, glucose, fructose have an effect on a savory and sweet taste.

In Korea, tea manufacturing and marketing are classified as three types; 1) some farmers produce fresh tea leaves, and sell them to manufacturing plants, 2) some manufacture in a home industry, and sell them directly 3) others produce fresh tea leaves in a home industry and sell them to consumers. Also, special product in a temple have been produced for self-consumption, and an excess of product have sold in markets.

However, regular transaction market in distribution structure has not been formed. So, production, circulation and consumption are not linked each other, and the price of tea product is relatively high and much different among tea manufacturers. The high quality teas have been sold to some of privileged classes with higher price and demand amounts are small, showing various quality criteria.

This research work has done in order to analyze and classify the characters related to tea quality, and offer basic information needed for standardization of tea products.

MATERIALS AND METHODS

A total of 43 samples of authentic green tea products in

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2002 were collected from Boseong, Jirisan, Gwangyang, Hwagae which were various in tea quality within the same manufacturer (Table 1) and stored at ambient temperature. Each sample was milled with a cyclone type mill and screened with a 200 mesh sieve to make particle size as even as possible. A multiple linear regression (MLR) has been developed by Jang Won Ind. (Seokwipo) and modified by our lab. All sample were scanned at ambient temperature using the near infrared (NIR) spectrophotometer (Model 6500, Foss NIRSystems, Intrasoft International LLC, USA)

Table 1. Entry numbers and green tea production companies collected from the southern regions of Korea

		- Legions (n Korea
Entry number	Green tea produce company	Entry number	Green tea produce company
1	BGT (5 ^z)	23	TS (5)
2	KTG (5)	24	TS (3)
3	DTG (5)	25	TS (1)
4	BTG (5)	26	HMT (5)
5	DOT (5)	27	HMT (3)
6	CTG (5)	28	JP (5)
7	BOT (5)	29	JP (3)
8	ETG (5)	30	JP (1)
9	BGT (3)	31	GD (5)
10	BGT (1)	32	GD (3)
11	KTG (3)	33	HMT (5)
12	KTG (1)	34	HMT (3)
13	DTG (3)	35	HMT (1)
14	DTG (1)	36	HN (5)
15	BTG (3)	37	JC (5)
16	BTG (1)	38	IGT (5)
17	DOT (3)	39	SGT (5)
18	DOT (1)	40	JJG (5)
19	CTG (3)	41	DOS (5)
20	CTG(1)	42	DOS (3)
21	BOT (3)	43	DOS (1)
22	BOT (1)	_	

we have arbitrarily weighed the values of 5 (1st grade), 3 (2nd grade) and 1 (3rd grade) according to picking times, respectively

with the reflectance unit fitted, scanning over the 400 - 2500 nm ranges at 32 resolutions per scan, giving 1050 data points for each spectrum (Choi et al., 2001; Kim et al., 1997). About 5 g of powdered green tea was packed into a closed cup and scanned. Three separate subsample were taken for each green tea. Eight chemical constituents were analyzed by NIR system to classify 43 green tea products.

RESULTS AND DISCUSSION

Variation of chemical components for green tea quality

The chemical components of green tea products which were produced, manufactured and sold by green tea manufacturers in the southern regions of Korea were shown in Table 2. The moisture content ranged from 2.18% to 5.97% with a mean of 3.7%, and coefficient of variation (CV) was 27.6% with great variation among green tea products. The total nitrogen content ranged from 441% to 6.42% with a mean of 5.63% and CV of 8.2%, and caffeine content ranged from 2.40% to 3 94% with a mean of 3.38% and CV of 10.9%. The catechins content ranged from 12 77% to 15.57% with a mean of 13.7% and CV of 4.7% with small variation among green tea products. The total free amino acid content ranged from 2.20% to 4.21% with a mean of 3.17% and CV of 15.8%. The theanine content among amino acids ranged from 0.90% to 2.28% with a mean of 1.64% and CV of 20.1% with the greatest variation among green tea products The ash content of green tea ranged from 10.53% to 22.04% with a mean of 1496% and CV of 17.7%, and vitamin C content ranged from 172.0 mg% to 305.38 mg% with a mean of 249.86 mg% and CV of 12.5%. The variation of moisture content among chemical components was the greatest (27.6%) followed by theanine (20.1%), ash (17.7%) and total free amino acid (15.8%). However, the variations of catechins and total nitrogen contents were relatively small, and this results suggested that the contents of catechins and total nitrogen were not greatly various according to different tea qualities. The chemical components of commercial green tea products used were various among production sites, green tea products, picking times

Table 2. The means, ranges, standard deviations (SD) and coefficient of variation (CV) in the several chemical components of green tea products with NIR analysis (n=43).

	Moisture (%)	Total nitrogen (%)	Caffeine (%)	Catechin (%)	Total free amino acid (%)	Theamne (%)	Ash(%)	Vitamin C (mg/100g)
Mean±SD	3 70±1 02	5 63±0.46	3 38±0 37	13.70±0.65	3 17±0 50	1 64±0 33	14 96±2.65	249 86±31 34
Range	2.18~5.97	4.41~6.42	2.40~3.94	12.77~15 57	2 20~4 21	0.90~2.28	10 53~22 04	172 00~305.38
CV(%)	27.6	8.2	109	47	15.8	20.1	177	12.5

and raw-materials (Park *et al.*, 1995, 1996; Kim *et al.*, 2002). Those results were similar to reports by Masuda *et al.* (1977), and Nakagawa & Furuya (1975).

Classification of green tea products

In this work shown as Table 3, the first and second principal components were 5.04 and 1.93, respectively, explaining the variation of 87%. The first component included moisture, vitamin C and catechins, and the second component included theanine, total free amino acids, and total nitrogen, showing a little difference in research work for tea germplasm done by Chun *et al.* (2003).

The principal component analyses of chemical components in 43 green tea products revealed 8 groups (Fig. 1). The first group included 16 products (1, 9, 10, 11, 12, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 27), the second group 5 products (2, 31, 36, 41, 42), the third group 13 products (3, 4, 5, 7, 8, 17, 25, 26, 32, 33, 34, 35, 43), the IV group 4 products

Table 3. Eigenvalues and their proportions obtained with principal component analysis.

Component	Eigenvalue	Difference	Proportion	Cumulative
Prin 1	5.038	3 110	0 630	0 630
Prin2	1 927	1.253	0.241	0 871
Prin3	0 674	0 379	0 084	0 955
Prin4	0.296	0 256	0 037	0 992
Prin5	0.040	0 026	0.005	0.997
Prin6	0 014	0.006	0.002	0.999

(28, 37, 38, 39), the V group 1 product (6), the VI group 2 products (29, 30), the VII group 1 product (40), the VIII group 1 product (18), respectively. In general, the first group included 37.2%, the third group 30.2%, the second group 11.6%, and the IV group 9.3%, respectively.

A cluster analyses based on 8 chemical components by UPGMA method revealed 8 groups that were similar to principal component analysis (Fig 2). Also, the averaged values of 8 chemical components per classified group by the cluster analysis were shown in Table 4. The first group included 16 products that had the traits with a little lower total free amino acids, but higher ash and vitamin C. The second group included 5 products that had the traits with higher total nitrogen, free amino acids, theanine and vitamin C, but lower moisture and ash. The third group included 13 products having the traits with the averaged values of chemical components in all green tea products. The IV group had higher moisture content, free amino acids and theanine, but lower ash and vitamin C. The V group had the highest moisture content, and a little high vitamin C content. The VI group included 2 products that had the traits with higher moisture, caffeine and catechins, but lower amino acids, theanine, ash and vitamin C. The VII group had especially high moisture and catechins contents, but much lower ash and vitamin C The VIII group had especially higher ash and vitamin C, but much lower contents of other components.

In general, the first group had a little contents of free amino acids and theanine, the second group had higher free amino acid and theanine, but lower ash content. The IV group had a little higher contents of moisture, free amino acids, and theanine, but lower ash and vitamin C. The V

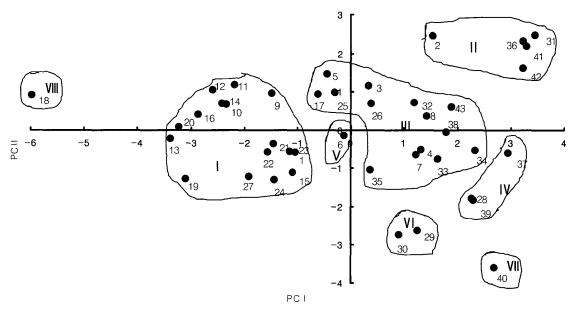


Fig. 1. Scattered plot of 43 green tea products classified by principal component analysis of chemical components

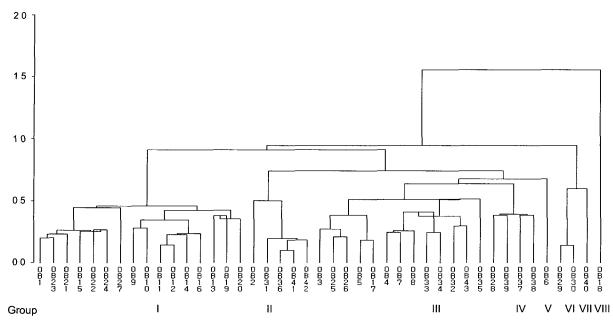


Fig. 2. Dendrogram of 43 green tea products classified by cluster analysis of chemical components using UPGMA method

Table 4. The mean values of 8 chemical components per classified group in 43 green tea products

Variable	Group								
variable	I (16)	II (5)	III (13)	IV (4)	V(1)	VI (2)	VII (1)	VIII (1)	
Moisture (%)	3.55	2 58	3 45	5 35	5 79	4 59	5 81	2 41	
Total nitrogen (%)	5 21	6.22	5 83	5 99	5.64	5 64	5 80	4.41	
Caffeine (%)	3 06	3 80	3 49	3.77	3.29	3 71	3 94	2.40	
Catechin (%)	13.45	13.37	13 85	13.73	12 92	15 50	15.25	12.78	
Total free amino acid (%)	2 72	4 08	3.37	3 58	3 24	2 82	3 18	2 20	
Theanine (%)	1.34	2 22	1 77	1 90	1 70	1.56	1 74	0.90	
Ash (%)	17 40	11 39	14 01	12.45	14 96	13 55	11.88	22 04	
Vitamin C (mg/100g)	260.99	261.63	248.78	210 51	264.88	220 72	172 00	305 38	

(): number of lines.

group had higher moisture, but much lower catechins, the VI group had higher moisture, and catechin, but lower free amino acid and theanine contents. The VII group had much higher moisture and catechins, the VIII group had much higher ash and vitamin C.

As shown in Fig. 1 and 2, some components of green tea products manufactured by the same manufacturers were various with different picking times except products of 2 manufacturers (in general, first-class, medium and low quality according to picking times), and they were classified into different groups. Those results suggested that the chemical components were changed with green tea raw-materials, picking times, or processing methods in each manufacturer. Those works have offered us good informations for the state of chemical components of present green tea products in the southern regions, and needs for standardization of green tea production.

Relationships among chemical components

The relationships among chemical components of green tea products are shown in Table 5. The moisture content (X_1) did positively correlate with catechins (0.323^*) , but negatively correlate with vitamin C content (-0.562^{**}) The total nitrogen content (X_2) had highly positive correlations with the free amino acids (0.956^{**}) , theanine (0.981^{**}) , and caffeine (0.919^{**}) , but negative correlations with ash (-0.969^{**}) and vitamin C contents, respectively The caffeine content (X_4) had highly positive correlations with theanine (0.858^{**}) , free amino acids (0.793^{**}) , and catechins (0.498^{**}) , but negative correlations with vitamin C content. The catechins content had negative correlations with vitamin C (-0.615^{**}) . The free amino acid (X_6) had positive correlations with theanine content (0.981^{**}) . The first principal component had positive correlations with caffeine, total nitrogen, theanine, free

Table 5. Simple correlation coefficients among chemical components of green tea products with NIR analysis (n=43).

				-	-	-		-		
Variable	X_2	X_3	X_4	X_5	X_6	\overline{X}_7	X ₈	X ₉	X ₁₀	X ₁₁
Moisture (X ₁)	0.022	-0 196	0.229	0 323*	-0.066	-0.040	-0 562**	0 194	-0 746**	0 292
Total nıtrogen (X2)		-0 969**	0 919**	0 232	0 956**	0 981**	-0 356*	0.970**	0.232	0.567**
Ash (X_3)			-0.966**	-0.418**	-0 884**	-0.927**	0 499**	-0 994**	-0.013	-0 582**
Caffeine (X ₄)				0 498**	0.793**	0 858**	-0.636**	0.977**	-0 121	0.521**
Catechin (X ₅)					0.011	0 127	-0.615**	0.409**	-0.689**	0.099
Total free amino acid (X_6)						0 981**	-0.177	0.887**	0.425**	0 576**
Theanine (X_7)							-0 237	0.930**	0.349*	0 577**
Vitamine $C(X_8)$								-0.545**	0 725**	-0.267
$Prin1(X_9)$									0	_
$Prin2 (X_{10})$										_
Quality $(X_{11})^{\dagger}$						_				

Prin1 and Prin2 calculated from principal component analysis, **, *Significant at the 0.01 and 0.05 probability levels, respectively. † classification of green tea quality by green tea products followed as . the best(5), medium(3), and the low(1).

amino acids, and catechins contents, the second principal component had positive correlations with vitamin C, free amino acids, theanine, respectively.

In general, green tea manufacturers classified green tea products as the finest goods (Ujeon), 1st grade (Sejag), 2nd grade (Jungjag), and 3rd grade (Daejag) according to earliness of picking tea leaves. The earlier the picking time is, the higher the green tea quality class is. Therefore, the importance of high quality of green tea is dependent on earliness of picking time.

So, we have weighed the values of 5 (1st grade), 3 (2nd grade) and 1 (3rd grade), respectively, and calculated correlations with chemical components. The overall quality (X_{11}) did positively correlate with the total nitrogen (0.567**), free amino acid (0.576**), theanine (0.577**), and caffeine (0.521**), but negatively with ash content (-0.582**), respectively. The free amino acid content that is the most important in flavor of evaluation of green tea quality did highly positively correlate with total nitrogen (0.956**), theanine (0.981**), caffeine contents (0.793**), but negatively with ash content (-0.884**), respectively. Also, the catechins content that is important as functional compound did positively correlate with caffeine content.

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