

Off-flavor Components of Green Tea during Preservation

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The total production of tea in the world was 2,218 thousand tons in 1984³⁾, and most part of the production was fermented tea such as black tea and oolong tea. There are not so much changes in flavor during the preservation of fermented tea¹⁵⁾, because easily oxidizable materials or compounds in tea leaves have already been oxidized during manufacturing²⁾.

The production of tea in Japan was 955 hundred tons in 1985, and most part of the production was green tea²⁾, non-fermented tea, which are manufactured through the first process of fresh leaf steaming in order to inactivate oxidative enzymes and to maintain green color. The production of fermented tea was only 1 ton in 1985.

The off-flavor easily occurred with the oxidation of materials in tea during preservation because of less oxidation during green tea manufacturing. The off-flavor of green tea smells strikingly, as compared to fermented tea, because the amount of aroma of green tea was less than that of fermented tea¹⁷⁾. Therefore, it has been the most important problem to prevent the off-flavor of green tea during preservation. The nitrogen packed packaging and low temperature preservation effectively prevent green tea from the occurrence of the off-flavor^{4-6,12)}, but the problem on the off-flavor formation by autooxidation or photooxidation in retail stores still remain unsolved.

From the above reasons, we investigated off-flavor components of green tea formed during preservation or storage under different con-

ditions of packaging or light-exposure by GC and GC-MS analyses of aroma concentrates prepared from off-flavor teas and by sensory evaluation of the teas.

Changes of aroma components of green tea during storage

Table 1 shows the amounts of aroma com-

Table 1. Changes in aroma components of green tea during storage

Components	Storage period (month)		
	0	2	4
1-Penten-3-ol	0.14	0.72	1.36
1-Pentanol	0.47	0.65	0.67
(Z)-2-Penten-1-ol	0.19	0.53	1.21
6-Methyl-5-hepten-2-one	0.29	0.58	1.08
1-Hexanol	0.22	0.78	1.47
(Z)-3-Hexen-1-ol	0.37	0.65	0.90
(E, Z)-2,4-Heptadienal	0.18	0.46	1.08
Linalool oxide (E)-furanoid	0.99	1.12	1.35
(E, E)-2,4-Heptadienal	0.20	0.52	0.95
1-Octanol	0.21	0.43	0.66
2,6,6-Trimethyl-2-hydroxycyclohexanone	0.88	0.96	1.43
β -Cyclocitral	0.66	0.85	1.19
α -Ionone	0.36	0.59	0.70
Geranylacetone	0.25	0.37	0.41
β -Ionone			
5,6-Epoxy- β -ionone			
Dihydroactinidiolide			

The values are the ratio of the peak area of each component to that of the internal standard (ethyl decanoate) on the gas chromatogram.

Storage conditions: green tea was packed in moisture proof pouches with air-enclosed packaging (initial moisture content, 4.5%), and stored in a dark chamber kept at 25°C and 75% relative humidity.

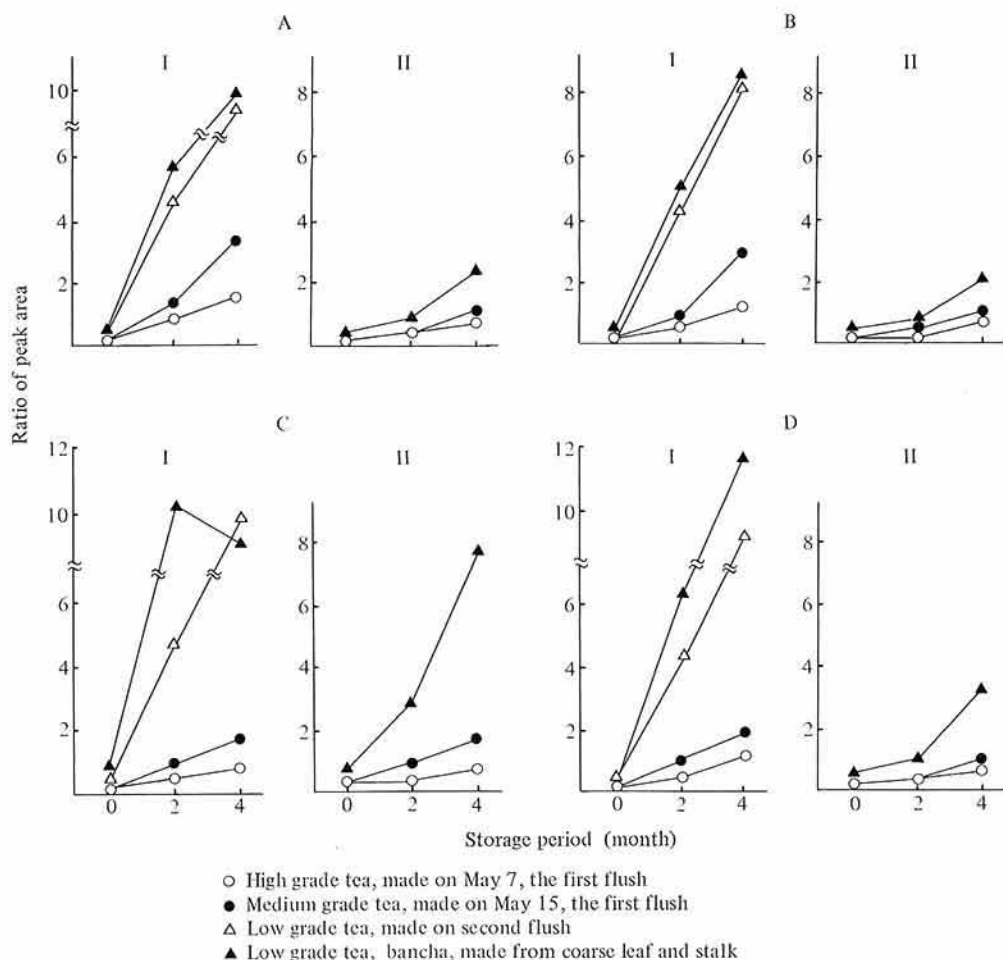


Fig. 1. Changes of four aroma compounds in green tea during storage
 A: 1-Penten-3-ol, B: (Z)-2-Penten-1-ol, C: (E, Z)-2, 4-Heptadienal,
 D: (E, E)-2, 4-Heptadienal.
 I: stored at 25°C, II: stored at 5°C.

ponents of fresh green tea (made on May 7, the first flush) and those stored for 2 months and 4 months. It is suspected that 1-penten-3-ol, 1-pentanol, (Z)-2-penten-1-ol, (Z)-3-hexen-1-ol and 2,4-heptadienals are oxidative degradation products of fatty acids^{9,16)} that are abundantly contained in tea¹⁾. The content of fatty acid decreases during storage¹⁾. Ionone derivatives (2,6,6-trimethyl-2-hydroxycyclohexanone, β -cyclocitral, α -ionone, β -ionone and dihydroactinidiolide), and 6-methyl-5-hepten-2-one and geranylacetone seem to be oxidative degradation products of

carotenoids¹⁸⁾.

Fig. 1 shows the changes in the contents of 1-penten-3-ol, (Z)-2-penten-1-ol, (E, Z)-2, 4-heptadienal and (E, E)-2,4-heptadienal during storage of four types of green teas¹⁹⁾. The longer the storage period or the lower the grade of tea, the more the increase in contents of these four components. These characteristics are common to other aroma components that increased during storage of green tea⁷⁾. The increase in these components during the storage at 5°C is small as compared to that during 25°C storage.

Table 2. Characterization of off-flavor which occurred during storage of packaged green tea

Storage period (month)	Moisture proof pouches ^{a)}				Ordinary pouches ^{b)} (air-enclosed packaging)	
	N ₂ -packed packaging		Air-enclosed packaging		Moisture content (%)	Sensory characteristics of flavor
	Moisture content (%)	Sensory characteristics of flavor	Moisture content (%)	Sensory characteristics of flavor		
1	2.7	Good tea aroma	2.7	good tea aroma	4.3	Good tea aroma
2	2.7	Good tea aroma	2.7	Slightly reversion flavor ^{c)}	5.5	Slightly deterioration flavor ^{d)}
3	2.7	Good tea aroma	2.7	Reversion flavor	6.6	Deterioration flavor
4	2.7	Good tea aroma	2.7	Reversion flavor	7.5	Deterioration flavor

Storage conditions: as described in Table 1, Initial moisture content: 2.7%.

a): Tea pouches for nitrogen packed packaging were employed.

b): Cellophane-polyethylene laminated tea pouches, not proof against moisture.

c): Reversion flavor; green notes.

d): Deterioration flavor; slightly acidic notes.

The occurrence of off-flavor components in packaged firing green tea during storage

The type of off-flavor which occurred during storage of firing green tea was different between moisture proof and non-proof (ordinary) pouches with air-enclosed packaging.

Table 2 shows the moisture content and sensory evaluation of flavor of packaged tea stored for 1 to 4 months, using moisture proof pouches or ordinary pouches with air-enclosed packaging and moisture proof pouches with nitrogen packed packaging.

When moisture proof pouches with nitrogen packed packaging were used, the moisture content and sensory evaluation of flavor of the tea did not change after 4 months of storage¹²⁾.

On the other hand, with moisture proof pouches with air-enclosed packaging, the reversion flavor having a green note occurred after the storage for 2 months, although the moisture content did not change for 4 months. When ordinary pouches with air-enclosed packaging were used, the moisture content increased gradually for 4 months, and deterioration flavor having an acidic note occurred in packaged firing green tea after the storage for 2 months.

Table 3 shows the occurrence of typical off-

flavor components during storage of firing green tea in moisture proof pouches with air enclosed packaging. All components except acetic acid, shown in Table 1 increased, and especially, 2,4-heptadienals remarkably.

Table 4 shows the changes of nitrogenous components⁸⁾ of firing green tea during storage. There are not so much changes during storage for 4 months. We presumed from the sensory evaluation that reversion flavor appeared as a result of disappearance of firing flavor, but from GC analysis, firing aroma components did not disappear. From the results shown in Tables 3 and 4, it is suspected that reversion flavor is the smell of off-flavor components such as 1-penten-3-ol, (Z)-2-

Table 3. The occurrence of off-flavor components during storage of firing green tea in moisture proof pouches

Components	Storage period (month)				
	0	1	2	3	4
1-Penten-3-ol	0.11	0.30	1.14	2.18	2.56
(Z)-2-Penten-1-ol	0.10	0.42	1.06	1.41	1.78
Acetic acid	0.42	0.39	0.52	0.78	0.94
(E, Z)-2,4-Heptadienal	0.34	0.92	1.80	3.15	4.50
(E, E)-2,4-Heptadienal	0.14	0.54	1.12	1.73	2.12

The values are as described in Table 1, but n-hexadecane was used as an internal standard. Storage conditions are as described in Table 1.

Table 4. Changes in nitrogenous components of firing green tea during storage in moisture proof pouches

Components	Storage period (month)			
	0	2	3	4
2-Methylpyrazine	0.43	0.42	0.42	0.43
2,5-Dimethylpyrazine	0.26	0.24	0.24	0.28
1-Ethyl-2-formylpyrrole	1.94	1.89	1.89	1.89
2-Acetylpyrrole	0.44	0.42	0.41	0.45

The values are as described in Table 1, but 2-acetylpyrazine was used as an internal standard. The same samples as used for Table 3 were injected into GC, but the compounds were detected with FTD (flame thermionic detector, specific and highly sensitive detector to nitrogenous compounds).

Table 5. The occurrence of off-flavor components during storage of firing green tea in ordinary pouches

Components	Storage period (month)				
	0	1	2	3	4
1-Penten-3-ol	0.11	0.62	0.58	0.68	1.08
(Z)-2-Penten-1-ol	0.10	0.38	0.46	0.57	0.98
Acetic acid	0.42	0.76	0.91	1.45	2.20
(E,Z)-2,4-Heptadienal	0.34	1.05	0.87	0.80	0.96
(E,E)-2,4-Heptadienal	0.14	0.47	0.52	0.56	0.63

The values: as described in Table 1.

Storage conditions: as described in Table 1.

penten-1-ol and 2,4-heptadienals, and these off-flavor components masked organoleptically the firing flavor.

Table 5 shows the formation of typical off-flavor components during storage of packaged firing green tea in ordinary pouches with air-enclosed packaging. All components increased, but the amount of increase was small as compared to that shown in Table 3, except acetic acid, that increased remarkably.

From these result, it is suspected that deterioration flavor having an acidic note is due to the remarkable increase of acetic acid.

The light-produced off-flavor components of the packaged green tea

The exposure of green tea to light (sun-

light, fluorescent lamps and other lamps) resulted in the occurrence of so-called sunlight flavor¹⁰). As green tea is sometimes packed in transparent pouches and placed on showcases under fluorescent lamps at retail stores, the occurrence of the sunlight flavor of green tea is also an important problem.

Table 6 shows changes of volatile components of green tea during exposure to light. Similar components to those shown in Table 1, such as 1-penten-3-ol, 1-pentanol, (Z)-2-penten-1-ol and 2,4-heptadienals, and 2,6,6-trimethyl-2-hydroxycyclohexanone, β -cyclocitral, α -ionone, β -ionone and dihydroactinidiolide, 6-methyl-5-hepten-2-one and geranylacetone are suspected to be the photooxidative degradation products of fatty acids^{7,9,16}) and carotenoids¹⁸).

On the other hand, pentanal, (E)-2-alkenals such as (E)-2-heptenal and (E)-2-decenal, C₈-alcohols such as 1-octen-3-ol and 2-octen-1-ol, bovolide and dihydrobovolide did not occur during storage in the dark⁷), and seemed to be produced only after exposure to light.

Among these components, bovolide showed the greatest amount of increase during exposure to light. It was produced even under the weak light condition (50 lx), and produced from black tea and semi-fermented tea. Hence, bovolide was thought to be an indicator to know whether tea had been exposed to light or not. But, organoleptically, bovolide has no sunlight flavor of green tea.

Table 7 shows the formation of volatile components from the mixture of linoleic acid and ether extracts of green tea after exposure to light. It is suspected that hexanal, (E)-2-heptenal and (E)-2-decenal might photooxidative degradation products of linoleic acid.

Alcohols such as 1-pentanol and 1-octanol were not regarded degradation compounds of linoleic acid.

The sunlight flavor of beer is due to sulphurous components¹⁴). As the sunlight flavor of green tea is stimulative, metallic and cabbage like odor¹³), the flavor also may be ascribed to sulphurous compounds.

However, these compounds cannot be recovered completely with steam distillation and

Table 6. Changes in volatile components of green tea during exposure to light

Compounds	Peak area		Compounds	Peak area	
	Control	Irradiated ^{a)}		Control	Irradiated ^{a)}
Alcohols			Ketones		
1-Penten-3-ol	0.38	1.00	6-Methyl-5-hepten-2-one	0.08	0.24
1-Pentanol	0.19	1.96	(E,Z)-3,5-Octadien-2-one	0.08	0.13
(Z)-2-Penten-1-ol	0.29	0.48	Geranyl acetone	0.18	0.40
1-Octen-3-ol	0.02	1.11	6,10,14-Trimethyl-2-pentadecanone	0.08	0.14
1,5-Octadien-3-ol	0.01	0.38	Ionone derivatives		
1-Octanol	0.50	0.85	2,6,6-Trimethylcyclohexanone	0.05	0.12
2-Octen-1-ol	0.03	0.86	2,6,6-Trimethyl-2-cyclohexenone	0.10	0.22
2,5-Octadien-1-ol	n.d. ^{b)}	0.52	2,6,6-Trimethyl-2-hydroxycyclohexanone	0.15	0.26
Alkanals			β -Cyclocitral	0.31	0.52
Pentanal	0.18	3.34	α -Ionone	0.11	0.24
Hexanal	0.28	1.05	β -Ionone	1.22	1.49
Nonanal	0.83	1.22	5,6-Epoxy- β -ionone	0.28	0.40
Alkenals			Dihydroactinidiolide	0.09	0.18
(E)-2-Heptenal	0.01	0.76	Bovolides		
(E)-2-Octenal	0.07	0.40	Bovolide	0.19	6.10
(E,Z)-2,4-Heptadienal	0.11	0.28	Dihydrobovolide	0.09	0.52
(E,E)-2,4-Heptadienal	0.10	0.57	Miscellaneous		
(E,E)-2,4-Octadienal	0.04	0.14	2-Pentylfuran	0.04	0.13
(E)-2-Decenal	0.16	0.92	Unknown (oxygenated compound C ₁₀ H ₁₈ O ₃)	0.18	2.68
(E)-2-Undecenal	n.d. ^{b)}	0.13			
(E,E)-2,4-Decadienal	0.01	0.21			

The values are as described in Table 1.

a): Exposure to light for 4 days under fluorescent lamp (approximately 2500 lx) at 25°C.

b): Not detected.

Table 7. Formation of volatile compounds from the mixture of linoleic acid and ether extracts of green tea after exposure to light

Components	Extracts alone	+Linoleic acid ^{a)}
Hexanal	4.64	11.16
(E)-2-Heptenal	2.84	5.38
(E)-2-Decenal	3.25	5.94
1-Pentanol	0.31	0.37
1-Octanol	0.79	0.67
2,5-Octadien-1-ol	0.29	0.24

The values are as described in Table 1 and corrected by calculation (irradiated values - control one).

Exposing conditions are as described in Table 6.

a): Added 0.1 g of linoleic acid per flask.

ether extraction methods^{7,10)}. Analysis will be done with a new method, headspace analysis¹¹⁾ using Tenax TA trapping system.

References

- 1) Anan, T.: The lipid of tea. *JARQ*, 16, 253-257 (1983).
- 2) Eden, T.: Tea. Longman, London, 153-196 (1976).
- 3) FAO production yearbook. 38, FAO, Rome (1984).
- 4) Fukatsu, S.: Nitrogen packaging of green tea by flexible packaging materials. *Study of Tea*, 45, 19-22 (1973) [In Japanese with English summary].
- 5) Fukatsu, S.: Storage of green tea by the use of various packaging. *JARQ*, 12, 33-38 (1978).
- 6) Furuya, K.: Inert gas packaging of tea. *JARQ*, 5(2), 45-49 (1970).
- 7) Hara, T. & Kubota, E.: Changes in aroma components of green tea after storage. *Nippon Nogeikagaku Kaishi*, 56, 625-630 (1982) [In Japanese with English summary].
- 8) Hara, T. & Kubota, E.: Changes in aroma components of green tea during the firing process. *Nippon Nogeikagaku Kaishi*, 58,

- 25-30 (1984) [In Japanese with English summary].
- 9) Hoffmann, G.: Isolation of two pairs of isomeric 2,4-alkadienals from soybean oil-reversion flavor concentrate. *J. Am. Oil Chem. Soc.*, 38, 31-32 (1961).
 - 10) Horita, H. et al.: The light-produced volatile components of green tea. *Agr. Biol. Chem.*, 49, 3601-3603 (1985).
 - 11) Horita, H. & Hara, T.: Analysis of head-space volatile components of tea using Tenax TA trapping system. *Study of Tea*, 68, 17-24 (1985) [In Japanese with English summary].
 - 12) Kubota, E. & Hara, T.: Shelf-life estimation and storage stability of packaged green tea. *Jpn. Packaging Res.*, 5, 5-10 (1985) [In Japanese with English summary].
 - 13) MacLeod, A.J. & MacLeod, G.: Effects of variations in cooking methods on the flavor volatiles of cabbage. *J. Food Sci.*, 35, 744-750 (1970).
 - 14) Obata, Y., Koshika, M. & Tanaka, H.: Studies on the sunlight flavor of beer. VIII. Mechanism of the formation of sunlight flavor. *Agr. Biol. Chem.*, 25, 588-593 (1961).
 - 15) Saijo, R. & Kuwabara, Y.: Gas chromatographic analysis of the head space vapor on black tea infusion. *Study of Tea*, 38, 11-18 (1969) [In Japanese with English summary].
 - 16) Sakurai, Y. & Arai, S.: Oxidative deterioration. In Food preservation. ed. Sakurai, Y., Mitsuta, H. & Shibasaki, K., Asakura Shoten, Tokyo, 230-284 (1966) [In Japanese].
 - 17) Takeo, T.: Variations in aromatic compound content in non-fermented and semi-fermented tea. *Nippon Nogeikagaku Kaishi*, 56, 799-801 (1982) [In Japanese with English summary].
 - 18) Yamaguchi, K. & Shibamoto, T.: Volatile constituents of green tea, Gyokuro (*Camellia sinensis* L. var. Yabukita). *J. Agr. Food Chem.*, 29, 366-370 (1981).
 - 19) Wickremasinghe, R.L.: Some observations on tea in Japan. *Tea Quarterly*, 39, 25-28 (1968).

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