

Comparison of the Odor Concentrates by SDE and Adsorptive Column Method from Green Tea Infusion

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The odor concentrates from green tea prepared by a simultaneous distillation and extraction (SDE) under reduced pressure and an adsorptive column method were investigated. A total of 218 compounds were quantified and identified by GC and GC-MS. Total concentrations were 92.9 ppm by SDE and 11.9 ppm by the column method. The concentrations of aliphatic alcohols and aldehydes were 7409 and 2681 ppb in the SDE concentrate and 241 and 108 ppb in the column concentrate, respectively. The concentrations of terpene alcohols were 8399 and 807 ppb, respectively. Most of ketones were found several times in the SDE concentrate compared with the column one. Further, large quantities of 1-propen-2-yl formate, pentyl formate and (*Z*)-3-hexenyl butanoate were formed during SDE, while 3-hexenyl hexanoate decreased. Coumaran, coumarin, vanillin, furanones, and lactones disappeared, while aromatic aldehydes, ionone derivatives, and indole were formed in quantity during SDE operation. SDE caused serious formations and decompositions of volatile compounds in green tea infusion, but the column method gave the odor concentrate with natural green tea flavor.

Keywords: Volatile compounds; green tea; Sen-cha

INTRODUCTION

Green tea is the most widely consumed beverage in Japan because of its pleasant flavor aside from its stimulating effect. Among green tea products, Sen-cha is the most popular one, representing over 80% of total production of green tea. Recently, its flavor has been used in pudding, cake, ice cream, soft drinks, etc. A canned green tea beverage is also manufactured commercially.

Volatile compounds of green tea have been investigated by many researchers, and over 300 volatile compounds have been reported (Yamanishi, 1978; Yamaguchi et al., 1981; Nguyen and Yamanishi, 1975; Hara and Horita, 1987; Hara and Kubota, 1982; Kawakami et al., 1991, 1981). These researchers have prepared the odor concentrate by a combination of steam distillation under reduced pressure and solvent extraction. It is, however, common knowledge that the flavor of green tea infusion is influenced sensitively by brewing temperature, brewing time, and quality of water, e.g. hardness and hypochloride concentration of tap water. Therefore, a method for separation and concentration of volatile compounds is a most important experimental factor for analysis of the volatile flavor compounds in green tea infusion.

In this study, a quantitative comparison of volatile compounds was carried out between the odor concentrates prepared by using a modified Likens-Nickerson apparatus (SDE method) under reduced pressure and those prepared by an adsorptive concentration method using a column packed with porous polymer beads.

MATERIALS AND METHODS

Green Tea. Fifteen Sen-cha products (*Camellia sinensis* L. var. Yabukita) of medium grade, based on market price, were obtained from The Tea Branch, Agricultural Institute of

Fukuoka Prefecture. Green tea samples were stored in a refrigerator (-20 °C) until analyzed.

Reagent. Methanol was passed through a column (35 mm × 500 mm) packed with an analytical grade active charcoal to remove impurities. Porous polymer beads, Porapak Q, were from Waters. All other reagents were analytical grade materials.

Adsorptive Column Method. Deionized hot water (80 °C, 1.0 L) was added to 50 g of Sen-cha, and the leaves were filtered by a coarse filter paper after standing for 3 min. The filtrate was immediately cooled to about 40 °C in tap water and passed through a column (28 mm × 250 mm) packed with 50 mL of Porapak Q. After the column was washed with 80 mL of deionized water, adsorbed compounds were eluted with a mixed solvent (80 mL) of diethyl ether and isopentane (1:1 v/v), which could elute volatile compounds quantitatively but did not elute polyphenols adsorbed on the column. On the other hand, with ether, polyphenols were eluted and obstructed preparing the odor concentrate for GC and GC-MS analysis (Shigematsu et al., 1994). The eluate was dried over anhydrous sodium sulfate for 12 h after the addition of internal standard (5.0 μL of 1.0% cyclohexanol), and the solvent was evaporated to about 1.0 mL. The adsorptive column could be regenerated by washing with ethyl ether (60 mL), purified methanol (80 mL), and deionized water (80 mL). Fifteen batches of Sen-cha samples were successively treated by this method (total amount treated = 750 g). The concentrated eluates were put together, and further concentration was conducted to about 200 μL.

Modified Likens-Nickerson Method (SDE Method). A sample (200 g) from the mixture of 15 batches of Sen-cha products was placed in a 2-L round-bottom flask, and deionized water (1.0 L) was added. Ethyl ether (70 mL) was used as an extracting solvent, and a SDE head was attached. The separation of volatile compounds was carried out under reduced pressure (150 mmHg, 70 °C) for 50 min. The condenser of the SDE head was cooled with a mixture of water and ethylene glycol at -5 °C. After the addition of internal standard (20 μL of 1.0% cyclohexanol), the extract was dried over anhydrous sodium sulfate and concentrated to about 100 μL.

Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS). A Shimadzu GC-14A equipped with a 60 m × 0.25 mm i.d. DB-Wax, film thickness 0.25 μm, fused silica capillary column (J&W Scientific, Folsom,

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CA) and a flame ionization detector (FID) was used. The oven temperature was programmed from 50 to 230 °C at 2 °C/min. The injector and detector temperatures were 200 and 250 °C, respectively. The flow rate of helium carrier gas was 26 cm³/s. A JEOL Automass 50 mass spectrometer interfaced with a Hewlett-Packard Model 5890 series II gas chromatograph was used for the identification of GC components. The column and oven conditions for GC-MS analysis were as described for GC analysis. Retention indices were estimated in accordance with a modified Kovats method (Van den Dool and Kratz, 1963) and compared with reported values. The mass spectra of the unknown compounds were compared with those in the NIST data base of the Automass 50 system and other published spectra (*Eight Peak Index of Mass Spectra*, 1983; Wiley/NBS *Registry of Mass Spectral Data*, 1989).

Preparative GC and Sniffing. To evaluate odor attributes of GC peaks, a preparative GC and sniffing was done (Shimoda et al., 1993) with the SDE and column concentrate. For preparative GC, a Shimadzu GC 8A was used, equipped with a 40 m × 1.2 mm i.d. chemically bonded PEG 20M (film thickness 1 μm) megabore open tubular column (Chemical Inspection and Testing Institute, Tokyo) and an FID. The oven temperature was programmed from 50 to 220 °C at 2 °C/min. Helium carrier gas flow rate was 18 mL/min with a splitless injection. Short capillaries (25 cm × 0.53 mm i.d.) with a chemically bonded phase of PEG 20M were used for trapping separated fractions or components with a split ratio of 20:1. The separated compounds were eluted on a filter paper with a drop of ethyl ether, and the odor was sniffed by two trained members.

RESULTS

In this study, the combined concentrates of volatile compounds from the 15 Sen-cha products were applied to GC and GC-MS analysis to obtain a typical composition of volatile flavor compounds of a medium grade Sen-cha. The odor concentrate by the column adsorptive method had a pleasant green tea odor with fresh, brisk, and sweet odor attributes, but that by the SDE method had a boiled green tea odor with woody, astringent, and stinging green odor attributes. Table 1 lists the identified compounds and quantitative values, which were calculated from peak area ratios to internal standard and related to the weight of Sen-cha product. A total of 218 compounds were definitely or tentatively identified including 38 alcohols, 28 aldehydes, 52 ketones, 20 esters, 9 acids, 4 phenols, 6 miscellaneous oxygenated compounds, 22 nitrogenous compounds, and 39 hydrocarbons.

The area of these identified peaks represented above 96% of the chromatogram surfaces (excluding solvent and cyclohexanol) of the SDE and column concentrates. The total concentrations of the identified compounds were 92.9 ppm by the SDE method and 11.9 ppm by the column method, respectively.

Among alcohols, aliphatic compounds were increased about 30 times by the SDE operation. The wide increases in saturated alcohols such as *n*-hexanol, *n*-octanol, and *n*-nonanol could be responsible for the woody and fragrant odors of the SDE concentrate. On the other hand, unsaturated alcohols except for (*E*)-3-hexen-1-ol were contained only in trace amounts in the column concentrate, but during the SDE operation (*Z*)-3-hexen-1-ol and (*E*)-2-octenol increased to 5517 and 258 ppb, respectively. Such great increases in unsaturated alcohols must impart a stinging green odor to the SDE concentrate. Takei et al. (1976) have described that (*Z*)-3-hexen-1-ol and its esters were responsible for the freshness and briskness of early spring green tea. We considered, however, unsaturated alcohols could have degraded the odor of Sen-cha infusion in their high levels. 2,6-Dimethyl-1,3,7-octatrien-6-ol (trienol) was formed from 2,6-dimethyl-3,7-octadiene-2,6-diol (diene-

diol) during a firing process (Hara et al., 1987). It was also reported that the former had a citrus-like and slightly fragrant odor and the latter had a weak citrus and green odor, though neither compound was found in the SDE concentrate. Hydroxybenzene alcohols were formed in large quantities during SDE, while benzene alcohols disappeared. The hydroxy compounds, which are not found in either green, partially fermented, or black tea, might be derived from a degradation of lignin in the tea product. All four types of linalool oxides increased by SDE, although *cis*-pyranoid was at almost the same level in both concentrates. Linalool, geraniol, *D*-nerolidol, and cadinols were also formed in large quantities during SDE. These terpene alcohols including linalool oxides have floral, woody, and rose-like pleasant odors (Belitz and Grosch, 1987a), but the great increases could result in a significant change in green tea odor. Especially the vast quantity of *D*-nerolidol could be responsible for woody and floral odors (Mossandl, 1992) of boiled green tea infusion.

Aliphatic aldehydes increased about 26 times by SDE: *n*-pentanal, *n*-hexanal, *n*-heptanal, (*Z*)-2-pentenal, (*Z*)-3-hexenal, (*Z*)-4-heptenal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E,Z*)- and (*E,E*)-2,4-heptadienal, and 2,6-dimethyl-5-heptenal were increased markedly. It was clear that these compounds could impart grassy and oily aldehydic odors to the SDE concentrate. Among aromatic aldehydes, principal components, which were benzaldehyde with a strong almond-like odor (*Atlas of Odor Character Profiles*, 1985) and benzeneacetaldehyde with a floral odor (Belitz and Grosch, 1987b), increased several times by SDE.

Most aliphatic and alicyclic ketones increased several times by SDE. Many kinds of alkenyl-2-ones, the characteristic group in the volatile compounds of green tea, could be liberated from free fatty acids which were first oxidized to β-keto acids and then decarboxylated to the corresponding ketones (Hawke, 1966; Forss, 1979). It was noted that 2,2,6-trimethylcyclohexanone, 3,5,5-trimethyl-2-cyclohexen-1-one, cyclohexanone derivative (*I*^{DB-Wax} = 1619), 4-ethyl-3,4-dimethyl-2,5-cyclohexadien-1-one, and 4-hydroxy-3,5,6-trimethyl-4-(3-oxo-1-butenyl)-2-cyclohexen-1-one, which were all degradation products of carotenoids (Kawashima, 1973), were formed in large quantities during SDE. The quantitative changes in aliphatic and alicyclic ketones having woody and hay-like odors must result in a great difference between two odor concentrates. Phenylethanone was formed during the SDE operation, while its two derivatives have disappeared. 1-(3,4-Dimethylphenyl)ethanone and 1-(4-ethylphenyl)ethanone have not been found in green tea, possibly owing to their lability in a green tea infusion. Preparative GC and sniffing of column concentrate showed the fraction from 1820 to 1920 in Kovats index had a typical green-tea-like odor, and authentic 1-(3,4-dimethylphenyl)ethanone and 1-(4-ethylphenyl)ethanone possessed a green-tea-like aroma with fragrant and sweet odors. Therefore, it was ascertained that the odor of green tea infusion was improved by the addition of 1-(3,4-dimethylphenyl)ethanone at a level of 100 ppb. The contents of these two compounds in the infusion of higher grade Sen-cha, however, were lower than those in medium grade Sen-cha infusion. It was considered that these compounds were the character impact compounds of green tea but that the quantitative balance of volatile flavor compounds was more important. 3-Keto-β-ionone and 7,8-dihydro-β-ionone exceptionally decreased, but β-ionone and other derivatives widely increased by SDE. The increases in β-ionone and its epoxides could be respon-

Table 1. Identification and Comparative Quantification of Volatile Compounds Separated from Green Tea

<i>I</i> ^{DB-Wax}	compound	approx concn, ^a μg/kg		<i>I</i> ^{DB-Wax}	compound	approx concn, ^a μg/kg	
		column ^b	SDE ^c			column ^b	SDE ^c
I. Alcohols							
1. Aliphatics				2. Aromatics			
912	2-propanol	241	7409	321	47212	221	175
925	ethanol	tr ^d	22	1870	benzenemethanol	35	tr
1083	2-methyl-1-propanol	tr	106	1903	benzeneethanol	65	tr
1136	<i>n</i> -butanol	tr	tr	1918	α-methyl-3-(1-methylethyl)benzeneethanol	tr	1866
1324	2-penten-1-ol	53	146	2257	3-hydroxybenzenemethanol	tr	4658
1345	<i>n</i> -hexanol	tr	161	2265	4-hydroxybenzenemethanol	tr	40513
1367	(<i>E</i>)-3-hexen-1-ol	27	42	2415	3-hydroxybenzeneethanol	807	8399
1383	(<i>Z</i>)-3-hexen-1-ol	tr	5517	1432	linalool oxide (<i>trans</i> -furanoid)	tr	119
1428	2,3-epoxyhexanol	13	19	1458	linalool oxide (<i>cis</i> -furanoid)	28	156
1441	1-octen-3-ol	tr	tr	1545	linalool	40	933
1473	2-ethylhexan-1-ol	24	tr	1614	2,6-dimethyl-1,3,7-octatrien-6-ol	23	tr
1554	<i>n</i> -octanol	16	456	1685	α-terpineol	tr	tr
1605	(<i>E</i>)-2-octenol	tr	258	1724	linalool oxide (<i>trans</i> -pyranoid)	58	130
1619	2-(2-ethoxyethoxy)ethanol	15	tr	1751	linalool oxide (<i>cis</i> -pyranoid)	234	272
1621	1,2-ethanediol	tr	445	1805	nerol	tr	tr
1653	<i>n</i> -nonanol	tr	28	1841	geraniol	tr	451
1932	3-hexene-2,5-diol	93	tr	2023	D-nerolidol	275	5934
1962	<i>n</i> -dodecanol	tr	14	2051	2,6-dimethyl-3,7-octadiene-2,6-diol	149	tr
2314	1,2,3-propanetriol	tr	173	2165	<i>d</i> -cadinol	tr	56
2197	(-)- <i>d</i> -cadinol	tr	348				
II. Aldehydes							
1. Aliphatics				2. Aromatics			
807	2-methylpropanal	108	2681	1476	(<i>E,E</i>)-2,4-heptadienal	tr	519
903	2-methylbutanal	tr	65	1543	(<i>Z</i>)-2-nonenal	tr	19
906	3-methylbutanal	39	tr	1576	(<i>E,Z</i>)-2,6-nonadienal	tr	28
968	<i>n</i> -pentanal	39	tr	1616	(<i>E</i>)-2-decenal	tr	31
1073	<i>n</i> -hexanal	tr	99	1697	2,6-dimethyl-5-heptenal	tr	451
1125	(<i>Z</i>)-2-pentenal	17	306	1815	(<i>E,E</i>)-2,4-decadienal	tr	36
1177	<i>n</i> -heptanal	tr	62			75	281
1196	(<i>E</i>)-2-hexenal	13	473	1496	benzaldehyde	37	184
1215	(<i>Z</i>)-3-hexenal	tr	tr	1623	benzeneacetaldehyde	38	56
1243	(<i>Z</i>)-4-heptenal	tr	136	1663	2-hydroxybenzaldehyde	tr	19
1291	(<i>E</i>)-2-heptenal	tr	45	1705	2,5-dimethylbenzaldehyde	tr	22
1385	<i>n</i> -nonanal	tr	65			8	93
1425	(<i>E</i>)-2-octenal	tr	12	1430	2,6,6-trimethyl-2-cyclohexene-1-carboxaldehyde	tr	11
1457	(<i>E,Z</i>)-2,4-heptadienal	tr	85	1447	furfural	tr	82
		tr	249				
III. Ketones							
1. Aliphatics				2. Aromatics			
875	2-butanone	595	3221	2665	4-(5-hydroxy-2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one	tr	128
955	2,3-butanedione	37	42			107	36
978	3,3-dimethyl-2-butanone	tr	59			tr	36
1019	1-penten-3-one	7	tr	1632	phenylethanone	tr	36
1056	2,3-pentanedione	tr	39	1831	1-(3,4-dimethylphenyl)ethanone	74	tr
1083	5-hexen-2-one	tr	59	1867	1-(4-ethylphenyl)ethanone	33	tr
1121	3-penten-2-one	8	76			tr	173
1131	4-methyl-3-penten-2-one	12	107	1714	1,6-methano[10]annulen-11-one	tr	tr
1155	5-methyl-2-hexanone	40	263	1843	<i>trans</i> -geranyl acetone	tr	173
1162	2-heptanone	tr	351			372	1774
1314	cyclohexanone	tr	22	1840	γ-ionone	tr	116
1345	2-methyl-6-methylene-1,7-octadien-3-one	193	22	1896	β-ionone-5,6-epoxide (<i>trans</i> type)	tr	45
1351	4-hydroxy-4-methyl-2-pentanone	tr	130	1942	β-ionone	tr	1157
1377	2,2,6-trimethylcyclohexanone	7	tr	2007	β-ionone-5,6-epoxide (<i>cis</i> type)	49	456
1387	6-methyl-5-hepten-2-one	tr	56	2068	6-methyl-α-ionone	84	tr
1406	3,5,5-trimethyl-2-cyclohexen-1-one	tr	133	2459	3-keto-β-ionone	tr	tr
1493	(<i>E,Z</i>)-3,5-octadien-2-one	tr	42	2653	7,8-dehydro-β-ionone	239	tr
1562	(<i>E,Z</i>)-3,5-octadien-2-one	35	102			264	tr
1564	2,6-dimethyl-2,5-heptadien-4-one	tr	65	1254	dihydro-3,5-dimethyl-2(3 <i>H</i>)-furanone	45	tr
1575	6-methyl-(<i>E,Z</i>)-3,5-heptadien-2-one	tr	tr	1671	dihydro-5-isopropyl-3(2 <i>H</i>)-furanone	21	tr
1582	6-methyl-(<i>E,E</i>)-3,5-heptadien-2-one	tr	tr	2034	dihydro-3-hydroxy-4,4-dimethyl-2(3 <i>H</i>)-furanone	7	tr
1619	cyclohexanone derivative	tr	31	2074	3,5,5-trimethyl-2(5 <i>H</i>)-furanone	19	tr
1629	4-ethyl-3,4-dimethyl-2,5-cyclohexadien-1-one	tr	391	2245	(<i>Z</i>)-7-decen-5-olide	172	tr
		tr	82			753	1062
1740	2,2,6-trimethyl-1,4-cyclohexanedione	tr	tr	1064	tetrahydro-3,6-dimethyl-2 <i>H</i> -pyran-2-one	21	tr
1778	2-(2-butoxyethoxy)ethanone	84	tr	1680	dihydro-3-methylene-2,5-furandione	tr	28
2067	3,5,5-trimethyl-4-(3-oxo-1-butenyl)-2-cyclohexen-1-one	113	tr	1952	3,4,4a,5,8,8a-hexahydro-4a-methyl-2(1 <i>H</i>)-naphthalenone	tr	859
2108	1,5-di- <i>tert</i> -butyl-3,3-dimethylbicyclo-[3.1.0]hexen-2-one	59	tr	1980	1-(1 <i>H</i> -pyrrol-2-yl)ethanone	186	25
2632	4-hydroxy-3,5,6-trimethyl-4-(3-oxo-1-butenyl)-2-cyclohexene-1-one	tr	1021	2260	3-ethyl-4-methyl-1 <i>H</i> -pyrrole-2,5-dione	285	tr
				2325	5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2(4 <i>H</i>)-benzofuranone	211	150
				2325			
IV. Esters							
1. Aliphatics				2. Aromatics			
851	1-methylethyl acetate	365	1577	1639	(<i>Z</i>)-3-hexenyl butanoate	tr	618
905	1-propen-2-yl formate	tr	tr	1819	dimethyl hexanedioate	tr	tr
969	methyl butanoate	tr	439	1850	3-hydroxy-2,4,4-trimethylpentyl 2-methylpropanoate	tr	76
				1882	2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl 2-methylpropanoate	14	133

Table 1 (Continued)

JDB-Wax	compound	approx concn, ^a µg/kg		JDB-Wax	compound	approx concn, ^a µg/kg	
		column ^b	SDE ^c			column ^b	SDE ^c
1059	butyl acetate	27	tr	1939	3-hexenyl hexanoate	295	tr
1258	pentyl formate	tr	221	2624	methyl linolenate	tr	59
1375	(Z)-3-hexenyl acetate	tr	tr		2. Others	210	158
1446	heptyl formate	tr	31	1763	methyl 2-hydroxybenzoate	tr	85
1612	(E)-3-hexenyl butanoate	tr	tr	2006	4-phenyl-2-butyl acetate	15	tr
1625	octyl 2-propenoate	tr	tr	2073	methyl 2-methoxybenzoate	12	tr
2338	methyl jasmonate	119	73				
					V. Acids		
	1. Aliphatics	1490	323	2157	n-nonanoic acid	340	tr
1435	acetic acid	171	312	2479	n-dodecanoic acid	81	tr
1833	n-hexanoic acid	224	tr	2679	n-tetradecanoic acid	6	
1943	n-heptanoic acid	457	tr		2. Aromatic Acid		
1954	3-hexenoic acid	211	tr	2521	benzeneacetic acid	81	tr
1969	2-ethylhexanoic acid	tr	11				
					VI. Phenolic Compounds		
1906	2,6-di-tert-butyl-p-cresol	3358	10133	2009	2-ethyl-4,5-dimethylphenol	88	tr
1987	2,5-diethylphenol	191	tr	2310	3,5-bis(1,1-dimethylethyl)phenol	tr	22
					VII. Miscellaneous Oxygenated Compounds		
833	tetrahydro-2-methylfuran	9		2389	coumaran	135	tr
1231	2-pentylfuran	tr	36	2451	coumarin	109	tr
1417	2-methoxy-1,3,5-trimethylbenzene	tr	22				
					VIII. Nitrogenous Compounds		
1184	1-ethyl-1H-pyrrole	tr	14	1660	isothiocyanatocyclohexane	tr	187
1282	methylpyrazine	tr	8	1691	N-butyl-N-nitroso-1-butanamine	tr	28
1372	2,5-dimethylpyrimidine	35	tr	1720	4-methoxybenzaldehyde oxime	16	tr
1381	2-ethyl-6-methylpyrazine	tr	tr	1746	N,N-dibutylformamide	tr	tr
1383	2-ethyl-5-methylpyrazine	tr	tr	1776	N,N-bis(1-methylethyl)-1,2-ethanediamine	tr	144
1414	N,N-dimethylacetamide	tr	17	1809	N,N-dibutylacetamide	tr	178
1439	3-ethyl-2,5-dimethylpyrazine	tr	tr	1863	(S)-3-(1-methyl-2-pyrrolidinyl)pyridine	tr	11
1479	methylhydrazine	18	tr	1912	2-methylbenzoxazole	17	tr
1490	1H-pyrrole	tr	14	1928	4-methylbenzoxazole	tr	198
1568	2-azido-2,3,3-trimethylbutane	5	tr	1955	benzisothiazole	tr	tr
1610	1-ethyl-1H-pyrrole-2-carboxaldehyde	35	490	1973	benzothiazole	tr	65
					IX. Hydrocarbons		
	1. Aliphatics	682	1000	1134	1,3-dimethylbenzene	25	17
800	n-octane	276	34	1190	1,2-dimethylbenzene	13	tr
823	4-methyloctane	22	tr	1205	1-methyl-2-ethylbenzene	585	tr
900	n-nonane	tr	tr	1207	n-propylbenzene	tr	28
1000	n-decane	51	34	1221	1-methyl-3-ethylbenzene	tr	422
1100	n-undecane	92	153	1227	1-methyl-4-ethylbenzene	tr	1762
1200	n-dodecane	tr	394	1250	1,3,5-trimethylbenzene	7	36
1263	(E)-2-dodecene	208	22	1278	1,2,4-trimethylbenzene	39	28
1269	bicyclo[4.2.0]octa-1,3,5-triene	tr	tr	1287	1-methyl-2-isopropylbenzene	tr	tr
1300	n-tridecane	12	tr	1296	1,3-diethylbenzene	21	tr
1365	3-methyltridecane	tr	14	1304	n-butylbenzene	33	130
1400	n-tetradecane	tr	5	1330	1-methyl-2-propylbenzene	tr	tr
1488	4,8-dimethyltridecane	tr	164	1351	bis(1-methylethyl)benzene	tr	39
1500	n-pentadecane	21	tr	1364	4-ethyl-1,2-dimethylbenzene	7	tr
1600	n-hexadecane	tr	90	1517	tetrahydronaphthalene	21	tr
1800	n-octadecane	tr	90	1572	1,3-butadienylbenzene	15	tr
1900	n-nonadecane	tr	tr	2228	3,4-diethyl-1,1'-biphenyl	43	tr
	2. Aromatics	832	2552		3. Terpenoids	70	229
1028	toluene	tr	90	1203	d-limonene	70	tr
1125	ethylbenzene	15	tr	1725	α-farnesene	tr	215
1130	1,4-dimethylbenzene	8	tr	1738	α-cubebene	tr	14

^a Only approximate concentrations since percent recoveries and FID response factors were not determined for each compound (assume all response factors of 1). ^b Adsorptive column concentration method. ^c Steam distillation continuous extraction under reduced pressure. ^d tr represents concentration less than 5 µg/kg.

sible for floral and fragrant odors (*Atlas of Odor Character Profiles*, 1985). Kawakami (1982) showed that ionone series compounds and cyclohexane derivatives were produced by thermal degradation of β-carotene. Besides the drastical increase of hexahydro-4a-methyl-2(1H)-naphthalenone by SDE, 3-ethyl-4-methyl-1H-pyrrole-2,5-dione, 3-ethyl-3-methyl-2,5-pyrrolidinedione, and 2H-1-benzopyran-2-one, which were confirmed to have an intense sweet odor by preparative GC and sniffing, almost disappeared by SDE. We concluded the disappearances of these compounds with sweet odor must definitely degrade the odor of green tea.

Among aliphatic esters, 3-hexenyl hexanoate, which was reported as an important contributor to the freshness of green tea (Takei et al., 1976; Kosuge et al., 1978),

decreased by SDE. On the other hand, a great deal of (E)-3-hexenyl butanoate and its two formates was formed by SDE. Although these esters have fresh and fruity odors, their formation in overly large quantities might impart an unnatural odor to the SDE concentrate.

The great increase in 1-ethyl-1H-pyrrole-2-carboxaldehyde was noted and seemed to be responsible for pungent and bitter odors. Isothiocyanatocyclohexane was responsible for a typical astringent odor of the SDE concentrate by preparative GC and sniffing. N,N-Bis-(1-methylethyl)-1,2-ethanediamine, N,N-dibutylacetamide, benzoxazoles, and other nitrogenous volatiles might impart unpleasant odors to the SDE concentrate.

It seemed that the disappearances of coumaran and vanillin seriously degraded the green tea odor; that is,

the odor concentrate by SDE possessed astringent and woody odors without any sweet odor attributes.

With respect to hydrocarbons, aromatic compounds increased about 3 times by SDE, and we concluded that the intense aromatic odor was not similar to a green tea odor. The disappearance of *d*-limonene and the formation of α -farnesene and α -cubebene were observed, although the sensory contribution would be low.

DISCUSSION

We have carried out a comparative investigation on the composition of volatile compounds from black tea (Shigematsu et al., 1994). It was shown that there were wide differences in the formation of volatile compounds during SDE between green tea and black tea. With regard to the SDE concentrate from black tea, a great increase in (*E*)-3-hexen-1-ol and decreases in *cis*- and *trans*-pyranoids of linalool oxides and β -ionone and its derivatives were observed. The increases in *n*-heptanol, *n*-octanol, D-nerolidol, and (*E,E*)- and (*E,Z*)-2,4-heptadienal were characteristic to green tea. The increase in *cis*- and *trans*-furanoids of linalool oxide and the decrease in α -terpineol and nerol were common to both teas.

Many authors (Hara and Kubota, 1982; Wright and Fishwick, 1979; Owuor et al., 1990) reported that aliphatic alcohols and aldehydes resulted from oxidative degradation of unsaturated fatty acid. We, however, ascertained few alcohols and aldehydes resulted from unsaturated fatty acids by SDE but they did result from the superoxides of unsaturated fatty acids. Although this is not reported yet, this is supported by the increase in the flavor reversion type off-flavor developing during storage (Horita, 1987). We also considered that the precursors of β -ionone, cyclohexanone, and cyclohexenone derivatives could be superoxides of carotenoids.

Kinugasa and Takeo (1990) reported that linalool, geraniol, D-nerolidol, and indole resulted from their glycosides in green tea infusion by pectinase. Takeoka et al. (1992) have reviewed that there were many kinds of glycosides of volatile compounds including benzaldehyde, benzene alcohols, and β -ionone and its derivatives in nectarine fruit. Therefore, it was clear that liberation of volatile compounds from nonvolatile glycosides by hydrolysis significantly influenced the chemical composition of the SDE odor concentrate.

It was concluded that the formations and decompositions of volatile compounds during SDE must bring about a serious difference in the flavor of green tea infusion, whereas the adsorptive column method enabled us to brew and separate volatile compounds in the same manner as we enjoy a green tea.

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