Flavor of Black Tea

Part II. Alcohols and Carbonyl Compounds

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The neutral fraction of the essential oils from three kinds of black tea (same samples as described in the previous paper,¹⁾ i.e., Assam, Shan and Benihomare) was separated into carbonyl and carbonyl-free fractions and analysed by gas chromatography. On the basis of relative retentions and aroma of effluents with the references of the chromatographic data obtained by the previous works,^{2~4)} the major alcohols were found to be *cis*-2-pentenol, *n*-hexanol, *cis*-3-hexen-1-ol, three isomers of linalooloxide, linalool, nerol, geraniol, benzylalcohol, and phenylethylalcohol. In the carbonyl fraction, phenylacetaldehyde was newly identified, and besides it, the presence of *iso*- and *n*-butyr-, *iso*- and *n*-valeraldehyde, methylethylketone, *trans*-2-hexenal, benzaldehyde were recognized. There were no differences in the components among three kinds of black tea, but the relative quantity of each component in the essential oil was different among three varieties.

INTRODUCTION

Surveys of the literature reveal rather few works on the essential oil of black tea. The most extensive investigation of the subject has been done by R. Yamamoto and Y. Kato⁵⁾ and S. Takei et al⁶⁾, and following alcohols and carbonyl compounds were identified. *n*-Hexyl-, *n*-octyl-, benzyl- and phenylethylalcohol, $\beta\gamma$ -hexenol, geraniol, linalool, *n*- and *iso*-butyraldehyde, *iso*-valeraldehyde, methylethylacetaldehyde, methylethylketone, benzaldehyde and $\alpha\beta$ -hexenal.

Recently, with the use of gas chromatography, three isomers of linalooloxide³⁾ and *cis*-2-pentenol⁴⁾ were identified from the essential

oil of black tea in this laboratory.

Since the neutral fraction of the essential oil of tea seems to be the main contribution to tea flavor, the neutral fraction was examined by gas chromatography.

The present paper reports the alcoholic and carbonyl constituents of the three kinds of black tea (i.e., Assam, Shan and Benihomare, same samples as described in the previous paper¹⁾) and differences of tea aroma among the three varieties based on the percent composition of alcohols and carbonyl compounds.

EXPERIMENTAL

Black Tea

The same three kinds of black tea as described in the previous paper¹⁾ were used.

The preparation of carbonyl- and carbonyl-free neutral fractions

The same crude essential oil as described in the previous paper¹⁾ was treated with 5% HCl and 5% NaOH successively to remove the basic and acidic fractions according to the routine procedure. The neutral fraction thus obtained was subjected to fur-

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2) T. Yamanishi, T. Kiribuchi, M. Sakai, N. Fujita, Y. Ikeda and K. Sasa, This Journal, **27**, 193 (1963).

3) T. Yamanishi, H. Sato and A. Ohmura, This Journal, **28**, 653 (1964).

4) A. Kobayashi, H. Sato and T. Yamanishi, This Journal, **29**, 487 (1965).

5) R. Yamamoto and Y. Kato, *J. Agr. Chem. Soc. Japan*, **10**, 661 (1934), **11**, 639 (1935), **13**, 736 (1937), **16**, 781 (1940).

6) S. Takei, Y. Sakato and M. Ohno, *Sci. Pap. I.P.C.R. Japan*, **14**, 303 (1935), **16**, 773 (1937), **17**, 871 (1938).

ther separation into carbonyl- and carbonyl-free fractions with Girard T reagent according to the method described by Teitelbaum.⁷⁾

Yields of the neutral fraction, carbonyl- and carbonyl-free-fractions from the crude essential oil are shown in Table I.

TABLE I. YIELDS OF THE NEUTRAL, CARBONYL AND CARBONYL-FREE FRACTIONS
(Percentage to Crude Essential Oil)

Fraction	Variety		
	Assam	Shan	Benihomare
Neutral	53.2%	45.2%	56.8%
Carbonyl-free	47.2	37.0	41.3
Carbonyl	6.0	8.2	15.5

Data show rather rough number since the crude essential oil and each fraction were not entirely ether free.

Gas Chromatography

Gas chromatography of both carbonyl- and carbonyl-free neutral fractions was conducted with Shimadzu Model GC-1C instrument equipped with thermal

conductivity detector. The column was 185 cm in length, 3 mm i.d., and packed with 23% Carbowax 6000 on 60~80 mesh Shimalite W and operated at 150°C under the helium flow rate of 20 ml per minute.

Peak Assignment and Quantitative Determination

Each peak on the chromatograms was assigned on the basis of identity in gas chromatographic data (i.e. relative retentions and aroma of effluent) with authentic compound.

Except the first four peaks, the relative quantity of each peak in carbonyl-free fraction was determined by calculating its percentage to total peak area.

As for carbonyl compounds, several peaks were trapped and subjected to infrared analyses. Quantitative determination by peak area was also carried out on several peaks.

RESULT AND DISCUSSION

As shown in Fig. 1, on the chromatograms of the carbonyl-free fraction, twenty-seven

FIG. 1. Gas Chromatograms of the Carbonyl-free Fractions.

7) C.L. Teitelbaum, *J. Org. Chem.*, **23**, 646 (1958).

peaks appeared over a period of eighty minutes. Among these peaks, fourteen peaks were identified as shown in Table II. The aroma of unidentified peak and the percentage of each peak area are also listed in Table II. In comparison of aroma pattern of three varieties, it was recognized that all three black tea contained the same kinds of alcohols but their composition were different especially in the proportion of linalool and three isomers of linalool oxide to geraniol, benzylalcohol and phenylethylalcohol. That is, Assam and Shan contain much more linalool and linalool-oxides and much less geraniol, benzylalcohol

and phenylethylalcohol than Benihomare.

As for the carbonyl fraction, more than twenty peaks obtained for fifty minutes run as shown in Fig. 2. From the relative retentions, *iso*- and *n*-butyraldehyde, *iso*- and *n*-valeraldehyde and methylethylketone were tentatively identified. Peak A, B and C in Fig. 2. were trapped by gas chromatography conducted under the same conditions using the Shimadzu Model GC-2A as described in the previous paper,²⁾ and examined by infrared analyses. Relative retentions and infrared spectra of peaks A, B and C were exactly same as those of authentic *trans*-2-hexenal,

TABLE II. CARBONYL-FREE NEUTRAL FRACTION OF THE ESSENTIAL OIL FROM THREE KINDS OF BLACK TEA (Reference to Fig. 1.)

Peak No.	<i>t</i> R _l	Peak Assignment and (Aroma) of Unidentified Peak	Peak area Percentage		
			Assam %	Shan %	Benihomare %
1	0.03				
2	0.04	Ether			
3	0.09	(Sweet aroma)			
4	0.12	(Sweet aroma)			
5	0.20	<i>n</i> -Butanol	3.7	1.2	4.1
6	0.25	<i>iso</i> -Pentanol	2.7	trace	0.8
7	0.32	(Unpleasant order of green note)	3.3	0.7	0.7
8	0.40	<i>cis</i> -2-Penten-1-ol	3.1	2.6	5.1
9	0.45	<i>n</i> -Hexanol	2.8	1.2	1.7
10	0.53	<i>cis</i> -3-Hexen-1-ol	8.2	7.8	5.0
11	0.68	(Woody arom)	trace	1.6	trace
12	0.76	Linalooloxide I	4.3	3.8	1.1
13	0.85	Linalooloxide II	9.2	17.9	2.0
14	1.00	Linalool	9.0	15.5	1.5
15	1.12	—	trace	0.6	trace
16	1.29	(Camphor like)	2.3	1.3	0.9
17	1.50	(Fresh trepang like)	1.7	0.6	trace
18	1.58		1.6	0.6	1.2
19	1.70	(Rose like)	1.2	0.7	trace
20	1.97	(Aroma, one of the contributions to good black tea flavor)	5.6	} 2.7	} 3.3
21	2.07		2.9		
22	2.28	Benzylacetate	3.4	4.8	3.3
23	2.43	Linalooloxide III	6.0	7.4	3.0
24	2.92	Nerol, with some contaminations	4.0	4.9	3.3
25	3.38	Geraniol	9.2	5.4	21.5
26	3.83	Benzylalcohol	8.8	11.2	24.3
27	4.43	Phenylethylalcohol	7.1	7.0	17.2

Note: *t*R_l means the relative retention time to linalool.

benzaldehyde and phenylacetaldehyde respectively. As phenylacetaldehyde has been never reported as a component of black tea flavor,

peak C was derived into 2,4-dinitrophenylhydrazone and confirmed by determination of melting point (mp. 121°C, same as authentic sample). The coincidence of infrared spectrum of peak C and authentic phenylacetaldehyde is shown in Fig. 3.

As shown in Table III, relative quantity of benzaldehyde is remarkably larger in Benihomare than in both Assam and Shan, whereas the components of shorter retentions than tR_i 0.31 are very small proportion in Benihomare compared with those of Assam and Shan.

FIG. 2. Gas Chromatograms of the Carbonyl Fractions.

TABLE III. CARBONYL FRACTION OF THE ESSENTIAL OIL FROM THREE KINDS OF BLACK TEA (Reference to Fig. 2.)

Peak tR_i	Peak Assignment	Peak Area Percentage		
		Assam %	Shan %	Benihomare %
0.09	<i>iso</i> -Butyraldehyde	66.8	60.3	25.8
0.10	<i>n</i> -Butyraldehyde			
0.11	Methylethylketone			
0.12	<i>iso</i> -Valeraldehyde			
0.14	<i>n</i> -Valeraldehyde			
	Unknown peaks			
0.31				
A 0.34	<i>trans</i> -2-Hexenal	2.3	2.7	3.7
B 1.13	Benzaldehyde	8.6	2.5	42.1
C 1.73	Phenylacetaldehyde	2.9	2.0	2.6

Note: tR_i means relative retentions to linalool.

FIG. 3. IR Spectra of Peak C (real line) and Authentic Phenylacetaldehyde (dotted line).

These facts may be also one of the causes of flavor differences between the varieties. There were many carbonyl compounds and also several non-carbonyl compounds remained unknown. Extensive research on these unknowns is now in progress in this laboratory.

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