

## Note

## Flavor Constituents of Pickled Tea, Miang, in Thailand

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Miang is a kind of pickled tea made in the northern part of Thailand and is known as "eating tea." This tea had been naturally fermented for three months in the manufacturing process without any preservatives such as sodium chloride. The product, however, has a typical pickled flavor: sour and flowery. We have also investigated the flavor of Japanese pickled teas, Goishi-cha and Awa-cha, which are used as usual for beverages.<sup>1)</sup> In this work, the characteristic flavor components of Miang are analyzed and their effects on Miang flavor is discussed. Also the effects of pickling on the development of tea aroma are investigated by comparing them with the aroma compositions of steamed tea leaves.

Fresh tea leaves (var. *Assamica*) were plucked in the Chiang Mai area (800 m above sea level) in Thailand in August, 1985. The samples in this work, "steamed tea leaves" and "fermented tea (Miang)" were manufactured as shown in Fig. 1.

One hundred grams of the steamed tea leaves and Miang were homogenized with 500 ml of water each and were distilled under reduced pressure (30 mmHg). During the distillation, 300 ml of water was added and the final distillate of about 750 ml was trapped in a cooled flask. The distillate was saturated with NaCl and extracted with ether. The preparation for the aroma concentrate was done as described in our previous paper<sup>2)</sup> (SDR method; Steam Distillation under Reduced Pressure Method). As a comparison of the aroma pattern between the SDR method and the SDE method (Simultaneous Distillation and Extraction method), Miang was also prepared using a modified Likens-Nickerson apparatus. Miang (50 g) was homogenized with 250 ml of water and was extracted with 50 ml of ether for 60 min.<sup>1)</sup> The aroma concentrates were analyzed using a Hewlett-Packard 5790 gas chromatograph coupled with a JEOL-JMS-DS 300 mass spec-

trometer. The MS data were analyzed by a JEOL-DA-5000 data processing system. Analytical conditions: Column, 50 m × 0.25 mm fused silica capillary column coated with FFAP. Column temperature, programed from 60°C, holds for 4 min, and up to 180°C at a rate of 2°C/min. Temperature of the injector and ion source were 200°C. The components were identified by matching their mass spectra and GC retention times with those of standard pure chemicals, and with our previous data<sup>1-5)</sup> or published MS data.

Gas chromatograms of the aroma concentrates from Miang and steamed tea leaves are shown in Fig. 2. The identified components and concentrations of each compound calculated by peak height percentage are listed in Table I. 3-Pentanol, (*E*)-4-hepten-2-ol, 2-methyl-3-thiacyclopentanone, 2-nonanol, neophytadiene, 1[7],8[10]-*p*-menthadiene-9-ol, and 4-propylguaiaicol are newly identified as components of the tea aroma. The main peaks in the aroma concentrate from steamed tea leaves are (*Z*)-3-hexenol, linalool, linalool oxide I, II, III, IV, and methyl salicylate. These compounds are present in fresh tea leaves in the form of precursors<sup>1)</sup> and seem to have been produced by tea leaf enzymes during the mild steam preparation.

After the fermentation process, various kinds of aroma components increased. The gas chromatogram of Miang by the SDE method is similar to that from the SDR method. Both sets of data shows that the aroma of Miang mainly consists of 11 components: (*Z*)-3-hexenol (peak 17), linalool (28), linalool oxide I (20), II (22), III (34), IV (35), methyl salicylate (36), benzyl alcohol (41), 2-phenylethanol (42), acetic acid (19), and 4-ethylphenol (56). The first 9 components are also common in pouchong and black teas<sup>4)</sup>. The last 2 components are typical in pickled tea, however.

The comparison of the aroma constituents grouped from their chemical structures between Miang and steamed tea leaves is shown in Fig. 3. As to acids, amounts of these compounds were 7.7~9.5% in the aroma concentrates of Miang. Acetic acid and other volatile acids showed their contribution to the pickled sour flavor. Aliphatic alcohols amount to 19.3~21.4% in the Miang aroma; especially secondary alcohols such as 2-butanol, 2-heptanol, (*E*)-4-hepten-2-ol, and 1-octen-3-ol increased considerably. These alcohols and acetoin seem to have been produced by microbial activity, and to have contributed to the fermented flavor. 1-Octen-3-ol has a strong moldy odor and was produced by mold.<sup>6)</sup> Aromatic alcohols such as benzyl alcohol and 2-phenylethanol also showed a great increase. Phenolic compounds are also present in large amounts. Lignin and coumaric acid seem to be the precursors of 4-ethylphenol, as in soy sauce.<sup>7)</sup> It seems to have been produced from coumaric acid through decarboxylation and hydrogenation of the double bond under the microbial reduced condition. 4-Methylguaiaicol, 4-ethylguaiaicol, 4-propylguaiaicol, and isoeugenol seem to be degradation products from ferulic acid,<sup>7)</sup> and it is

TABLE I. THE CONTENTS OF VOLATILE COMPOUNDS IN MIANG

Peak No.	$t_R$ (min)	Compound	Peak height (%)		
			Miang		Steamed leaves
			SDE	SDR	SDR
1	3'19''	Acetone	2.2	0.7	6.2
2	3 46	Butanone	2.2	3.8	
3	4 02	Ethanol	2.9	1.2	6.5
4	5 07	2-Butanol	7.1	7.9	
5	5 22	Propanol	2.6	2.4	
6	6 27	2-Methylpropanol	0.3	0.2	
7	6 51	3-Pentanol*	0.3	0.2	
8	9 26	2-Heptanone	0.3	0.8	3.4
9	10 10	2-Methylbutanol	0.3	0.4	
10	10 15	3-Methylbutanol	0.7	1.1	
11	12 07	Pentanol	0.2	0.2	
12	12 29	3-Octanone	0.1		0.7
13	13 36	Acetoin	2.2	1.7	
14	15 42	2-Heptanol	2.0	2.6	
14'		6-Methyl-5-heptene-2-one			2.1
15	15 49	3-Methyl-2-buten-1-ol	0.1	0.2	
16	16 51	( <i>E</i> )-4-Hepten-2-ol*	0.5	1.4	
16'		2-Nonanone			0.3
17	19 11	( <i>Z</i> )-3-Hexenol	3.9	3.4	1.0
18	19 53	3-Octanol	0.2	0.2	
19	21 40	Acetic acid	3.4	3.6	
20	22 26	Linalool oxide I ( <i>cis</i> , furanoid)	6.0	4.6	9.0
21	23 05	1-Octen-3-ol	0.7	1.1	
21'		( <i>E</i> )-2,( <i>E</i> )-4-Heptadienal			0.7
22	24 08	Linalool oxide II ( <i>trans</i> , furanoid)	8.1	8.0	12.8
23	25 29	2-Ethylhexane-1-ol	0.2		
24	26 45	Benzaldehyde	0.1		
25	27 04	2-Methyl-3-thia-cyclopentanone*	0.3	0.1	
26	27 24	2-Nonanol*	0.2	0.1	
27	27 33	Propionic acid	1.8	3.5	
28	29 07	Linalool	10.9	10.2	15.3
29	29 34	Isobutyric acid	0.3	0.5	
30	32 31	3,7-Dimethyl-1,5,7-octatrien-3-ol	0.3		0.3
30'		4-Terpineol			0.3
31	33 04	Butyric acid	0.3	0.4	
31'		Acetophenone			0.5
32	35 33	Isovaleric acid	0.2	0.3	
33	37 19	$\alpha$ -Terpineol	1.4	1.2	2.7
34	39 44	Linalool oxide III ( <i>cis</i> , pyranoid)	3.4	2.7	3.1
35	41 17	Linalool oxide IV ( <i>trans</i> , pyranoid)	8.6	7.4	10.2
36	41 27	Methyl salicyrate	5.7	5.2	14.5
37	43 25	Nerol	0.3	0.4	
38	43 56	Phenylethyl acetate	0.1	0.1	
39	45 28	Hexanoic acid	0.9	0.5	
40	46 06	Geraniol	1.2	1.0	0.3
41	46 58	Benzyl alcohol	2.4	4.7	0.2
42	48 52	2-Phenylethanol	4.3	5.5	1.7
43	49 38	B.H.T.			
43'		$\beta$ -Ionone			0.3
44	51 09	4-Methylguaiaacol	0.9	0.5	
45	51 19	( <i>Z</i> )-3-Hexenoic acid	0.5	0.7	

TABLE I. (continued)

Peak No.	$t_R$ (min)	Compound	Peak height (%)		
			Miang		Steamed leaves
			SDE	SDR	SDR
46	53 36	Phenol	0.5	1.7	3.1
47	53 52	Unknown-(aromatic compound $M^+ - 134$ )	0.1	0.1	
48	54 30	Neophytadiene*	0.1		
49	55 00	4-Ethylguaiacol	0.3	0.4	
50	55 36	1[7],8[10]- <i>p</i> -Menthadien-9-ol*	0.3	0.4	
51	56 22	Nerolidol	0.7		1.0
52	56 44	Octanoic acid	0.3		
52'		<i>p</i> -Cresol		t	0.7
52''		<i>o</i> -Cresol		0.1	0.7
53	58 59	4-Propylguaiacol*	0.2	0.2	
54	60 58	Bobolide + 6,10,14-trimethylpentadecanone	0.1	0.1	0.9
55	61 43	Isoeugenol	0.1		
		Theaspirone	0.1		1.4
56	62 04	4-Ethylphenol	6.4	6.4	
			99.9	100.0	99.9

\* Newly identified compounds.

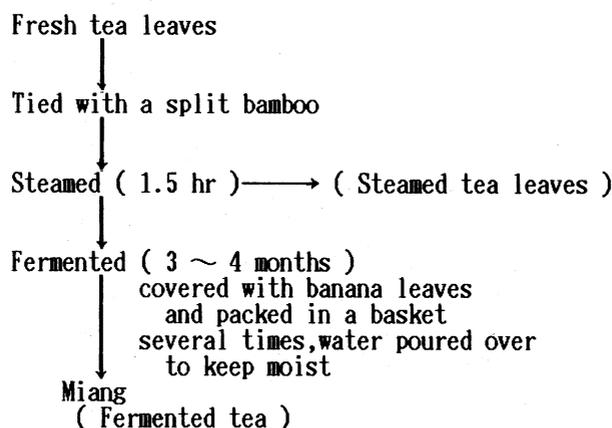


FIG. 1. Manufacturing Process of Miang.

presumed that these phenols are also produced by microbes and give a smoky flavor to the pickled tea.

Summarizing the above results, the aroma constituents of Miang can be divided into two groups. The first group originates in the enzymatic activity of tea leaves and the components are similar to those of semi-fermented tea; and the second group is the products from microbial activity during the pickling. These results agree with the results<sup>1)</sup> obtained from Japanese pickled tea, Goishi-cha and Awa-cha, which were dried after the pickling.

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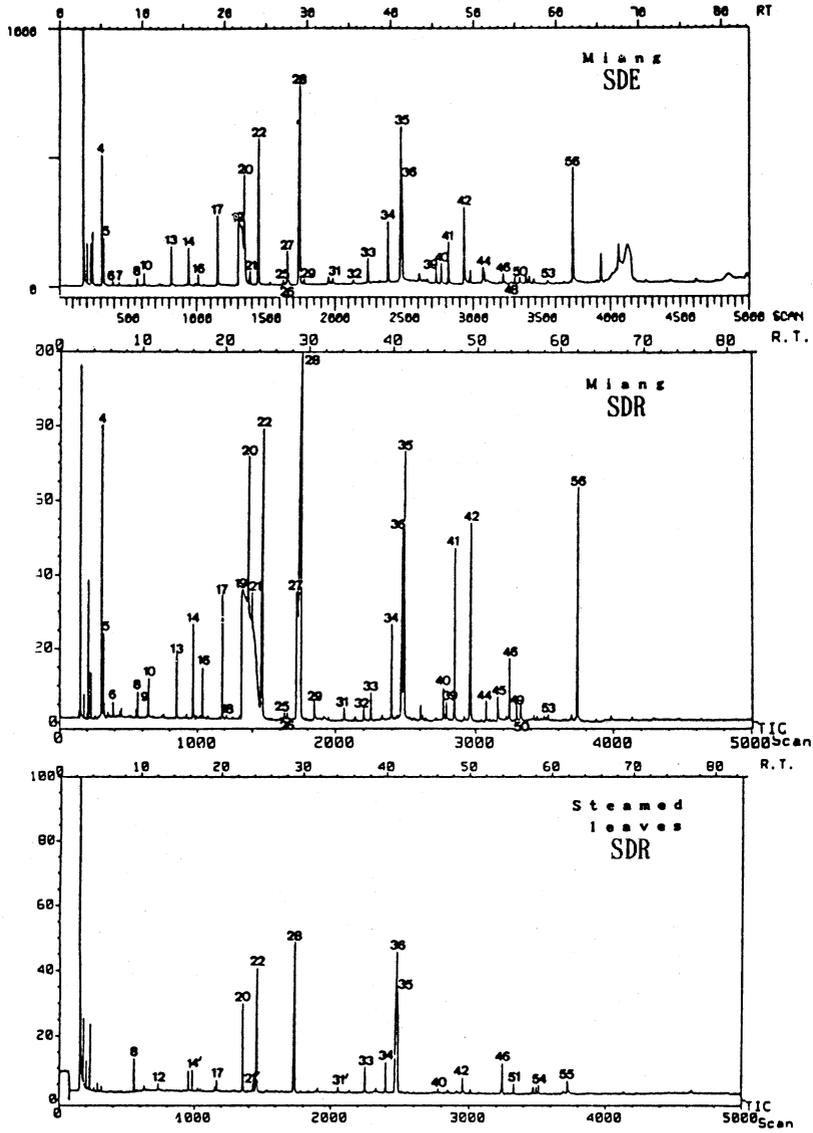


FIG. 2. Gas Chromatograms of Miang and Steamed Tea Leaves.

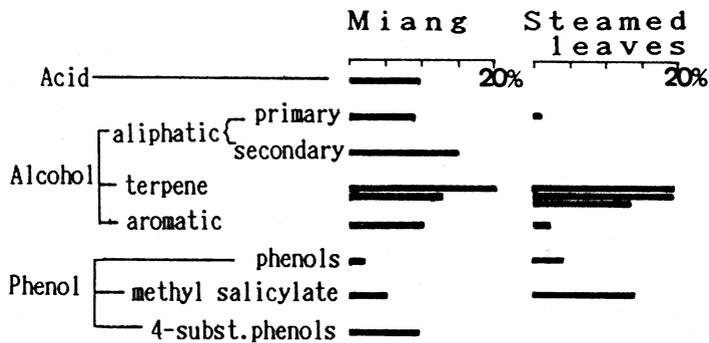


FIG. 3. Comparison of the Aroma Patterns between Miang and Steamed Tea Leaves.

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