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Changes of Volatile Components of Tomato Fruits During Ripening

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ABSTRACT

Volatile components obtained by simultaneous steam distillation–extraction from two varieties of tomato fruits at various ripening stages and their artificially ripened tomato fruits were analyzed by GC and GC–MS using a glass capillary column. One hundred and thirty compounds were identified. Of these, quantitative changes in the major thirty-six compounds were investigated. Hexanal, trans-*2-hexenal, 2-*iso-*butylthiazole, 2-methyl-2-hepten-6-one, geranylacetone and farnesylacetone, which were estimated to be important volatile components of fresh tomato aroma by the GC–Sniff method, increased with natural and artificial ripening. However, many volatile components showed complicated changes in the case of artificially ripened tomato fruits.*

INTRODUCTION

In a previous paper (Chung *et al.* 1983), the authors investigated the volatile components of ripe tomatoes and their juices, purées and pastes; the ripe tomatoes were of varieties used in processing. In Japan, the

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consumption of tomato fruits of varieties normally eaten raw is increasing. Usually, tomato fruits eaten raw are artificially ripened for several days, the balance of the harvest being kept for collection as cargo, for transportation, buying, selling, and so on. It is assumed that the chemical changes in tomato fruits during artificial ripening and storage have an effect upon the quality. Shah *et al.* (1969) indicated that the concentrations of short-chain (C4-C6) compounds were higher in the artificially ripened tomato fruits while the long-chain (C9-C12) carbonyls and the terpene esters were predominant in the field-ripe fruits. Therefore, they proposed that major contributions of the long-chain carbonyls and terpene esters are essential for ripe tomato aroma. There are, moreover, several papers concerning the volatile components of tomato fruits during ripening (Dalal *et al.*, 1967; Yu *et al.*, 1968). Kader *et al.* (1977) reported that tomatoes picked at earlier stages of ripeness and ripened at 20 °C were evaluated by panelists as being less sweet, more sour, less tomato-like and possessing more off-flavour than those picked at the table-ripe stage. However, they did not identify the flavour components.

In the present paper, the authors investigate the changes of volatile components in tomato fruits during various ripening stages and artificial ripening by using glass capillary column gas chromatography.

MATERIALS AND METHODS

Tomato fruits

Tomato fruits of two varieties, Horei and Satan, harvested at a farm at Chiba University, Chiba Prefecture, Japan, in 1980, were used. These varieties are eaten raw and not used for processing. Field-grown tomato fruits were classified into three ripening stages, according to the colour of the fruit's surface, as follows. Mature green: tomato fruits are fully grown and the fruit's surface is completely green. Turning: the part coloured to yellow or pink is 10–30 % of the fruit's surface. Light red: the part coloured to pink red or red is 69–90 % of the fruit's surface. These tomato fruits were washed and artificially fully ripened under darkness at 20 °C or natural light at 20 °C. Table 1 shows the average storage periods required for full ripening under two environmental conditions. These tomato fruits were stored at −20 °C until used.

TABLE 1
Average Storage Periods Required for Full Ripening Under Two Environmental Conditions

Ripening stage of fresh tomato fruits before storage		*Environmental conditions and storage periods (days) required for artificial ripening* A	B
1. Mature-green	(1)	6	5
	(2)	6	5
2. Turning	(1)	5	4
	(2)	5	4
3. Light-red	(1)	4	3
	(2)	4	3

A: 20 °C, dark room; B: 20 °C, natural light
(1): Horei (2): Satan

Preparation of volatile concentrate by simultaneous steam distillation–extraction (SDE)

The authors used the simultaneous steam distillation–extraction (SDE) apparatus described by Shultz *et al.* (1977) which was the modified apparatus of Nickerson & Likens (1966), in order to collect the volatile components from tomato fruits. One kilogram of crushed tomato fruits, 1 litre of distilled water and 500 μg of *n*-hexadecane dissolved in 10 ml of diethyl ether as internal standard were placed in a 3-litre flask. The 3-litre flask was joined to the riser of the SDE head. A 200-ml eggplant-shaped flask containing 100 ml of diethyl ether was connected to the other riser. SDE was carried out for 1·5 h and the resulting ether extract was concentrated at 36–38 °C under atmospheric pressure. The volatile components in the concentrate were analyzed by GC and GC–MS.

Gas chromatography (GC)

Each volatile concentrate obtained by SDE was analyzed with a Shimadzu Model 5A Gas Chromatograph equipped with a flame ionization detector (FID). A glass capillary column (60 m × 0·28 mm inside diameter) coated with PEG 20M was used. The column oven temperature was programmed from 60 °C to 190 °C at a rate of 4 °C/min. The injection port and detector temperature were kept at 200 °C. Nitrogen was used as the carrier gas at a flow rate of 1·5 ml/min with a split ratio of 1:15·3.

Gas chromatography–mass spectrometry (GC–MS)

GC–MS spectra were recorded with an Hitachi Model RM-50 Mass Spectrometer connected with an Hitachi Model 063 Gas Chromatograph. Ionization voltage was 25 eV and ion source temperature was kept at 200 °C. A glass capillary column (50 m × 0·28 mm inside diameter) coated with PEG 20M was used. The column oven temperature was programmed from 60 to 170 °C at a rate of 3 °C/min and the injection port temperature was 200 °C. The carrier gas (helium) was controlled at an inlet pressure of 0·2 kg/cm^2.

RESULTS AND DISCUSSION

Figure 1 shows the gas chromatograms of ripe tomato fruits (Horei and Satan) obtained by SDE. The volatile components were similar for both tomato fruits, even if quantitative differences between the two gas chromatographic patterns are considered.

The odor of the volatile components obtained by SDE was judged by sniffing the gas chromatography effluents as described in previous papers (Chuyen & Kato, 1982). From the results of sniffing for each volatile component eluted from the GC, some compounds reminiscent of green tomato odor were detected but no character-impact compound was found in any tomato fruit.

Volatile compounds identified in the present investigation are listed in Tables 2 and 3. One hundred and thirty compounds were identified. Of these, quantitative changes in thirty-six compounds at three ripening stages and two ripening conditions are shown in Table 2. Eighteen minor volatile compounds, which were not identified in tomato fruits used in processing, were identified, as shown in Table 3 (Chung *et al.*, 1983).

Changes of volatile components at various ripening stages of field-grown tomato fruits

In general, the relative amounts of most major volatile components obtained by SDE of field-grown tomato fruits increased with ripening, as

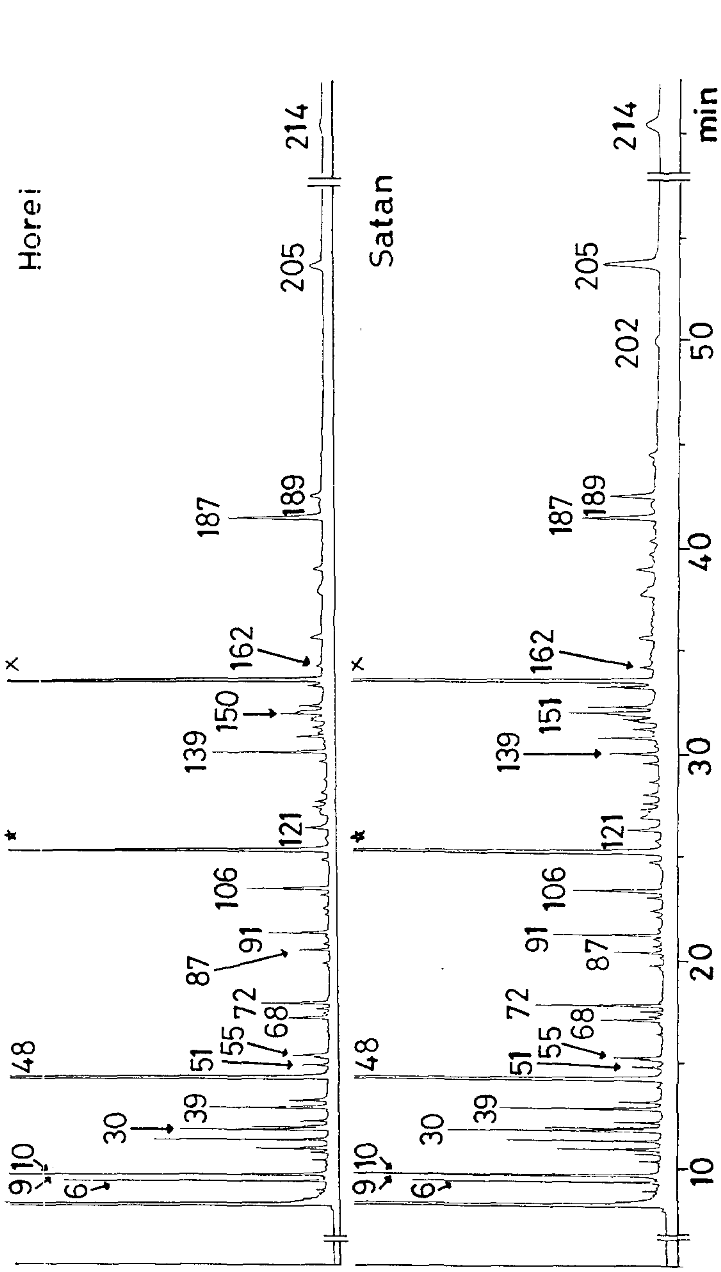

Fig. 1. Gas chromatograms of volatile components of Horei and Satan, which were artificially ripened from turning stage, obtained by simultaneous steam distillation–extraction. +: *n*-Hexadecane; ×: Butylated hydroxy toluene (BHT), a contaminant originating from ether used as the solvent.

TABLE 2
Relative Amounts* of Major Volatile Components Obtained by SDE from Fresh and Artificially Ripened Tomato Fruits

Peak no.	*Compounds*		*Fresh market tomato fruits of*			*(A)*			*(B)*		
			MG	*T*	*LR*	*MG*	*T*	*LR*	*MG*	*T*	*LR*
Hydrocarbons											
(24)	Toluene	(1)	18	15	22	15	10	7	13	9	9
		(2)	7	16	10	7	8	18	12	9	17
(38)	Ethylbenzene +	(1)	12	12	23	77	34	15	30	19	11
	1-Butanol	(2)	6	19	17	42	30	44	29	15	20
Alcohols											
(9)	Ethanol + 3-Methyl-	(1)	135	162	52	80	36	18	49	26	31
	1-butanal**	(2)	23	82	62	48	35	87	51	38	49
(19)	2-Butanol	(1)	1	1	3	15	13	9	13	5	6
		(2)	t	2	2	19	22	13	13	12	8
(21)	1-Propanol + 2-	(1)	14	13	15	54	17	7	18	11	7
	Methyl-3-buten-2-ol	(2)	4	13	10	25	13	23	15	10	10
(27′)	2-Methyl-1-	(1)	8	9	27	88	43	16	53	18	16
	propanol + 2-Hexanone	(2)	3	12	21	62	31	48	34	16	23
(32)	1-Propen-3-ol	(1)	1	5	4	44	23	4	19	8	2
		(2)	1	2	4	24	11	17	16	3	4
(48)	3-Methyl-1-butanol**	(1)	90	117	264	562	330	126	293	139	84
	+ Methyl hexanoate	(2)	49	107	204	412	202	319	239	82	136
(55)	1-Pentanol	(1)	6	6	8	14	9	5	7	8	5
		(2)	3	6	6	11	11	10	9	9	8
(90)	2-Methyl-2-hepten-	(1)	0	t	1	17	6	3	9	4	2
	6-ol	(2)	t	t	1	15	7	12	12	4	5
(106)	Linalool	(1)	19	17	21	17	16	10	17	12	11
		(2)	10	11	13	17	13	16	18	11	11
(122)	Furfuryl alcohol	(1)	5	6	7	19	15	7	15	10	7
	+ Phenylacetaldehyde	(2)	4	6	7	16	11	15	20	7	17
(158)	2-Phenylethanol	(1)	1	1	4	24	24	13	22	14	18
		(2)	1	2	7	19	9	16	23	10	33
Aldehydes											
(30)	Hexanal** +	(1)	6	6	11	13	10	7	11	12	8
	Dimethyldisulphide	(2)	3	6	9	9	13	16	15	13	12
(51)	*trans*-2-Hexenal	(1)	6	3	5	7	9	4	22	8	5
		(2)	1	3	3	3	7	6	23	9	9
(91)	2-Furfural	(1)	9	12	11	23	18	10	22	16	11
		(2)	5	9	11	19	16	18	26	12	16

TABLE 2—*contd.*

Peak no.	*Compounds*		*Fresh market tomato fruits of*			*(A)*			*(B)*		
			MG	*T*	*LR*	*MG*	*T*	*LR*	*MG*	*T*	*LR*
Aldehydes—contd.											
(144)	*t,t*-2,4-Decadienal +	(1)	5	6	10	12	16	11	14	11	12
	(147) *t,c*-2,4-Decadienal	(2)	6	10	14	12	18	16	14	16	14
Ketones											
(72)	2-Methyl-2-	(1)	1	2	15	52	48	25	61	37	19
	hepten-6-one	(2)	1	3	15	37	37	59	75	28	38
(151)	Geranylacetone	(1)	0	0	6	19	20	17	21	14	16
		(2)	0	0	10	12	18	17	16	15	14
(205)	Farnesylacetone	(1)	0	0	9	16	19	27	24	19	29
		(2)	0	0	22	10	22	24	16	33	24
Esters											
(6)	Ethyl acetate	(1)	40	43	28	46	30	12	40	24	17
		(2)	11	25	14	26	29	42	40	23	37
(68)	*trans*-2-Hexenylacetate	(1)	5	5	10	11	9	5	8	7	5
		(2)	3	7	8	8	7	9	8	6	8
(214)	Methyl linoleate	(1)	0	0	0	0	6	0	0	19	6
		(2)	0	0	0	7	7	0	0	29	0
Phenols											
(139)	Methyl salicylate	(1)	48	33	24	8	5	6	6	4	8
		(2)	25	32	6	8	14	4	7	7	7
(150)	Guaiacol	(1)	12	12	9	10	8	7	5	7	8
		(2)	8	16	5	9	15	4	8	7	8
(187)	Eugenol	(1)	22	35	37	29	46	38	25	26	51
		(2)	23	36	16	40	51	25	29	40	25
(189)	4-Vinylguaiacol	(1)	7	8	5	8	7	4	10	11	6
		(2)	8	9	10	10	6	7	6	5	3
Others											
(84)	2-*Iso*-butylthiazole	(1)	0	0	2	6	6	3	7	3	3
		(2)	0	0	2	4	6	6	10	4	5

(1) Horei and their artificially ripened tomato fruits.
(2) Satan and their artificially ripened tomato fruits.
(A) Tomato fruits ripened from MG (Mature-green), T (Turning) and LR (Light-red) at 20 °C in a dark room.
(B) Tomato fruits ripened from MG, T and LR at 20 °C under natural light.
* Peak area of *n*-Hexadecan used for internal standard = 100.
** Main compound in two components.
t: Trace.

TABLE 3
Minor Volatile Components Identified in Ripe Tomato Fruits

Peak no.	*Compounds*	*Peak no.*	*Compounds*	*Peak no.*	*Compounds*
Aromatic hydrocarbons		*Aldehydes*		*Esters*	
12	Benzene	1′	Acetaldehyde	2′	Methyl acetate
40	*p*-Xylene	4	2-Propenal	2	Ethyl formate
43	*m*-Xylene	7	Butanal	28	Butyl acetate*
47′	Cumene*	16	Pentanal	36	Amyl acetate*
50	1-Phenylpropane	37	*trans*-2-Pentenal*	69	*cis*-3-Hexenyl acetate
58	Styrene	65	Octanal	83′	Methyl octanoate
61	*p*-Cumene	71	*trans*-2-Heptenal	181	Methyl pentadecanoate
64	Pseudocumene	83	*trans,trans*-2,4-Hexadienal	193	Methyl palmitate
70	1-Phenylbutane*	87	*trans*-2-Octenal		
75	1,2,3-Trimethylbenzene	94	*trans,trans*-2,4-Heptadienal	*Furans*	
		97	Decanal	8	2-Methylfuran
Terpene hydrocarbons		103	Benzaldehyde	13	2-Ethylfuran
23	alpha-Pinene*	104	*trans*-2-Nonenal	54	2-Pentylfuran
31	Camphene*	119	Torualdehyde	57	1-Methyl-5-*iso*-propenylfuran
41	Sabinene	127	Neral	100	2-Acetylfuran
48	*d*-Limonene*	133	Geranial		
67	Terpinolene	140	Hydrocinnamaldehyde*	*Phenols*	
		173	*trans*-Cinnamaldehyde	142	*o*-Hydroxyacetophenone
				145	Ethyl salicylate

Alcohols
5 Methanol*
8′ Propan-2-ol*
33 Allyl alcohol*
42 1-Penten-3-ol
73 1-Hexanol
78 *cis*-3-Hexenol
82 *trans*-2-Hexanol
88 1-Octen-3-ol
88′ 1-Heptanol*
89 *trans*-Linalooloxide (furanoid)
108 *cis*-4-Hexenol
108′ 1-Octanol*
128 alpha-Terpineol
138 Citronellol
149 Geraniol
152 Benzyl alcohol

Ketones
1 Acetone
7 2-Butanone
14 Diacetyl
15 2-Pentanone*
35 3-Penten-2-one
46′ 2-Heptanone
47 Cyclopentanone
86 *trans,trans*-3,5-Octadien-6-one
113 2-Methyl-2,4-heptadien-6-one
162 beta-Ionone

Lactones
117 1,4-Butanolide*
188 2,4-Dimethyl-2-nonene-4-olide*
202 Dihydroactinidiolide

167′ *o*-Cresol
167 Phenol
204 4-Vinylphenol

Others
46 Pyridine
160 Phenylacetonitrile
183 *p*-Methoxyacetophenone

*Acids***
A-1 Acetic acid
A-2 Propionic acid
A-3 *Iso*-butyric acid
A-4 Butanoic acid
A-5 Valeric acid
A-6 Hexanoic acid
A-7 Heptanoic acid
A-8 Octanoic acid
A-9 Nonanoic acid
A-10 Benzoic acid
A-13 Palmitic acid

* Compounds identified only in ripe tomato fruits for raw consumption and not identified in tomato fruits for processing use as shown in previous paper (Chung *et al.*, 1983).
** The concentrate obtained by SDE was fractionated into neutral, basic, phenolic and acidic fractions. The acidic fraction was treated with diazomethane for methylation of the acids in the fraction.

shown in Table 2. The increasing amounts of the major volatile components of the two varieties, Horei and Satan, with ripening were similar. The amount of middle and high-boiling volatile alcohols and ketones increased between the turning and light red stages. This was especially pronounced with 2-methyl-1-propanol and 2-hexanone (peak 27′), 3-methyl-1-butanol (peak 48), 2-methyl-2-hepten-6-one (peak 72), geranylacetone (peak 151) and farnesylacetone (peak 205).

The flavour of tomato fruits is almost surely due to a blend of several aroma compounds, e.g. hexanal, *trans*-2-hexenal, *cis*-3-hexenal, *cis*-3-hexenol, 2-*iso*-butylthiazole, and so on (Nursten, 1979). *cis*-3-Hexenal has a freshly cut green tomato flavour and a low threshold, 0·25 ppb (Buttery *et al.*, 1971). It was not detected in the present investigation in the same manner as in the previous paper (Chung *et al.*, 1983). From the results of GC–Sniff analysis, volatile components important to fresh tomato aroma were found to be peak 30 (hexanal), peak 51 (*trans*-2-hexenal), peak 78 (*cis*-3-hexenol), peak 82 (*trans*-2-hexenol), peak 151 (geranylacetone) and peak 205 (farnesylacetone). Peak 84 (2-*iso*-butylthiazole) had a grassy and sweet fruity odour in the present sensory evaluation test by GC. Kazeniac & Hall (1970) reported that 2-*iso*-butylthiazole appeared to intensify the fresh tomato flavour note obtained with *cis*-3-hexenal. They also found that the pure 2-*iso*-butylthiazole in aqueous solution had a spoiled vine-like, slightly horseradish-type flavour, which was rather objectionable; however, when 2-*iso*-butylthiazole was added to canned tomato juice or tomato paste, it produced a more intense, fresh tomato-like flavour (Kazeniak & Hall, 1970). Guadagni *et al.* (1972) indicated that a mixture of *cis*-3-hexenal, 2-methyl-2-hepten-6-one, eugenol and beta-ionone significantly improved the aroma of tomato juice prepared from foam-mat-dried tomato powder. From the results and findings described above, the levels of 2-*iso*-butylthiazole and 2-methyl-2-hepten-6-one are considered to have an important rôle in fresh tomato aroma. In addition, the remarkable increases of geranylacetone and farnesylacetone will have important effects on the aroma. Some of these components are probably formed from unsaturated fatty acids and polyene carotenes (Eriksson, 1979; Stevens, 1970).

Dalal *et al.* (1967) observed the increase of carbonyl compounds with ripening. They also noted that the concentration of 3-methyl-1-butanal was maximum at the breaker stage of maturation. These findings are similar to those of the present investigation. It is known that a crude enzyme solution prepared from green tomatoes synthesizes 3-methyl-1-butanal, using leucine as the substrate (Yu *et al.*, 1968).

The relative amounts of methyl salicylate and guaiacol decreased in the light-red stage, as shown in Table 2. It is considered that some metabolic changes accompany the formation of these phenols with ripening of the tomato fruits.

Changes of volatile components during artificial ripening of tomato fruits

Table 2 shows the relative amounts of major volatile components contained in the SDE of artificially ripened tomato fruits. Relatíve amounts in mature green (MG), turning (T) and light red (LR) stages increased, respectively, with artificial ripening at 20 °C in the dark room or under natural light. Especially, 2-butanol, 2-phenylethanol, 2-methyl-2-hepten-6-one, geranylacetone, farnesylacetone and 2-*iso*-butylthiazole increased with aritificial ripening. 3-Methyl-1-butanal, however, decreased under some artificial ripening conditions. This finding accorded with the result of the change of 3-methyl-1-butanal at three ripening stages of field-grown tomato fruits. Methyl salicylate also decreased with artificial ripening from MG and T.

There are some differences between ripening in a dark room and under natural light. Many low-boiling alcohols such as 1-propanol and 3-methyl-1-butanol increased more in the case of artificial ripening from the MG and T stages in the dark compared with exposure to natural light. Comparing the relative amounts of volatile components in artificially ripened tomato fruits from three ripening stages under dark and natural light conditions, these changes were complicated by the difference in volatile components between tomato varieties.

Generally, the intact tissue of vegetables contains only non-volatile precursors, which are separated from appropriate enzymes (Tressl *et al.*, 1975). Many volatile components in vegetables such as tomato, celery and cucumber are formed from non-volatile precursors when the tissues are destroyed during homogenization, heating, and so on. These reactions are enzyme catalyzed. Consequently, it is considered that the changes of the volatile components in tomato fruits with natural and artificial ripening depend on the intensity of the various enzymatic activities in intact tissue and the accumulation of substrates, especially the enzymatic synthesis of C6 and C9 compounds from fatty acids, ketones from carotenoids and aldehydes and alcohols from amino acids.

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