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Improvement of the Flavor of Canned Satsuma Mandarin with the Essence

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The aim of the present study is to improve flavor of the canned Satsuma mandarin by supplement of the essence which was prepared from cold-pressed oil of flavedo. The volatile compounds of fresh juice sacs, the essence and the canned Satsuma mandarin were isolated by simultaneous distillation and extraction under reduced pressure, and analyzed with a GC-MS. Linalool was not detected in the canned Satsuma mandarin without the essence after four months at 37℃. On the other hand, linalool was maintained in high concentration in the canned Satsuma mandarin with the essence after four months at 37℃. Furthermore, some volatile compounds of the essence kept in the canned Satsuma mandarin, such as α-pinene, limonene, citronellol, perillaldehyde, 1-octanol, hexanal, and octanal and so on. As a result, the freshness of the canned Satsuma mandarin has been maintained. In the sense evaluation, most of panelists preferred the canned Satsuma mandarin with the essence to one without the essence.

Key words : aroma, canned fruit, essence, flavor, GC-MS, Satsuma mandarin, volatile compounds.

INTRODUCTION

Satsuma mandarin has outer peel (flavedo), albedo, segment and juice sacs. The flavedo has oil glands containing essencial oil. The juice sacs are the only material of canned Satsuma mandarin. The canned Satsuma mandarin does not need the flavedo. Accordingly, the canned Satsuma mandarin hardly has essencial oil. The flavor of the canned Satsuma mandarin is poorer than that of Satsuma mandarin juice extracted commercially. The terpenoids may contribute to the flavor of the canned Satsuma madarin. Predominant aroma compounds in the canned Satsuma mandarin were limonene and linalool (1). Some volatiles considerably disappeared by canning, and gradually decreased during the course of storage. Flavoring is done with the canned drink (2). Since flavoring is hardly done for the canned Satsuma mandarin, we already tried to improve the flavor of the canned Satsuma mandarin with cold-pressed oil which was extracted from the peel (3). Those canned Satsuma mandarin gave out the strong smell of terpenoids. An excess of terpenoids may not be suitable for the canned Satsuma mandarin. Subsequently, we prepared the essence by removing almost terpenoids from cold-pressed oil. The present study aims to improve the flavor of the canned Satsuma mandarin with the essence.

注　本論文は *Applied Biological Science*, 7 (2001) 49－56 掲載論文を転載したものです．

MATERIALS AND METHODS

Materials

The Satsuma mandarin (*Citrus unshiu* MARC. cv. Miyagawa-wase) produced in Kumamoto prefecture were purchased from a fruit market. The concentration of soluble solids, pH and citric acid were 9.4 °Brix, 3.4 and 0.6%, respectively, in the fresh Satsuma mandarin. The essence, which was prepared from cold-pressed oil by elimination of 95% terpenoids was obtained from Shionokoryo Ltd.

Sample Preparation

(1) The preparation of fresh Satsuma mandarin juice sacs

Satsuma mandarin were immersed in 90℃ hot water for one minute in order to soften the outer peel. The outer peel was removed by hand. After removal of the peel, the fruit was separated into segments by hand. The segments soaked in 0.7% hydrochloric acid solution at 40℃ for 27min with occasional stirring. The weight ratio of 0.7% hydrochloric acid solution to segments was 4 to 3. They were washed by running water and soaked in 0.3% sodium hydroxide solution at 40℃ for 4min with stirring. The weight ratio of 0.3% sodium hydroxide solution to segments was 4 to 3. After chemical treatment, they were fully washed with water and then they were washed with running water for 60min. The segment membranes were dissolved by chemical treatment to get fresh juice sacs. The concentration of soluble solids, pH and citric acid of fresh juice sacs were 8.3 °Brix, 3.6 and 0.6%, respectively. The volatile compounds of fresh juice sacs were isolated by simultaneous distillation and extraction under reduced pressure (RSDE).

(2) Processing procedures for the canned Satsuma mandarin

Steel cans were filled by hand with fresh juice sacs (275g). The cans were made from plain electrolytic plate and recommended for canned Satsuma mandarin. The concentration of the sugar syrup was determined based on the sugar content of fresh juice sacs. The canned fruits were left stand two weeks to equalize the syrup to the desired Brix degree, about 14 °Brix degree. The sugar syrup of 23.5 °Brix degree (165g/can) was filled to get 14 °Brix degree. The concentration of citric acid was 0.025% in the sugar syrup. The sugar syrup was added at a temperature of 90℃. The total weight of contents was 440g. The essence was not added to the control. The cans were closed by 5M vacuum closer. The gauge of chamber vacuum was fitted to -62kPa. The canned Satsuma mandarin were subjected to low temperature pasteurization by a rotary sterilizer at a bath temperature of 80℃ for 10min at the rate of 5rpm. Immediately after pasteurization, the cans were cooled until the average temperature of the contents reached to 40℃ by a water cooling bath. The cans were stored at room temperature (15~25℃) or were thermostated at 37±2℃ for use for analysis.

(3) Processing procedures for the canned Satsuma mandarin with the essence

Processing procedures are as follows: Fresh juice sacs (275g) were filled into can by hand and then added 440mg of the essence. The total weight of contents was 440g by the addition of the sugar syrup as described above. The cans were closed, pasteurized and cooled in the same way as the control cans, and stored at the room temperature or were thermostated at 37±2℃.

(4) The extraction and concentration of the volatile compounds

We prepared the apparatus called simultaneous distillation and extraction (SDE) head as described previously (4). The SDE system is used for isolating volatiles from agricultural products. The volatile compounds from fresh juice sacs, the essence and canned Satsuma mandarin were isolated by the method of RSDE with the SDE system. Samples were taken in a 2L flask. The 2L flask was joined to the left-hand riser of the SDE head, and a 100mL flask containing 50mL of high purity dichloromethane was connected to the other riser. When temperature of the 2L flask reached to 65℃, the reducing valve was closed. The volatile compounds of each sample were isolated with the SDE system for 2 hours at constant pressure. Cyclohexanol of 1mg was dissolved in dichloromethane of 1mL. This cyclohexanol solution of 200μL was added to the extracted solution as an internal standard. The solution was dehydrated by shaking with sodium sulfate anhydrous. The solution was concentrated to 500μL by the Kuderna-Danish apparatus, then to 100μL by blowing nitrogen gas in a freezing mixture with sodium chloride and ice. The volatile compounds concentration of each sample was measured. Six samples prepared for the RSDE were as follows.

Fresh juice sacs of 550g were put in a 2L flask, then added, the syrup of 330g, and ultra pure water of 500mL were added. Also essence of 880mg was put in a 2L flask, and ultra pure water of 500mL was added. All of four kinds of the canned samples as described below were used from two canned fruits, and ultra pure water of 500mL was added in a 2L flask. The canned Satsuma mandarin stored for one month at room temperature. The canned Satsuma mandarin with the essence stored for one month at room temperature. The canned Satsuma mandarin stored for four monhs at 37℃. The canned Satsuma mandarin with the essence stored for four months at 37℃. Volatile compounds were determined by the extraction from these samples. Volumes of 3μL were injected to determine with GC-MS.

(5) Analysis of the volatile compounds

Mass spectra were obtained on a Hewlett-Packard 6890 GC/MSD system with a fused silica polar capillary column coated with DB-Wax (J&W Scientific, Inc.,0.25mm i.d.$\times$60m, film thickness 0.25μm). The operating conditions were as follows: helium (Zero-U) carrier, rate of line (25cm/sec); a split ratio of 20 : 1; the injector temperature 260℃. The column temperature was held at 40℃ for 5min, then programmed to 200℃ at 3℃/min, and held there for 30min. The transfer line temperature was 250℃. Mass spectra were obtained from electron ionization energy at 70eV and within the mass range of m/z 10 ~ 300. We used the Hewlett Packard Chemistation System for the analysis of the data and searched the library database of the National Bureau of Standards. Results of qualitative analysis were verified by comparison of mass spectral data and Kovats index with those of authentic reference substances. Eight compounds were identified referring to retention indices which were reported by Sakamoto (5). The internal standard used for the experiments was cyclohexanol. Concentrations were calculated from total ion intensity by internal standard method without response correction. The weight of the total juice sacs of two cans was 550g. We calculated, therefore, concentration of the volatile compounds according to the sample as 550g.

(6) The paired preference test

Forty-eight persons were used as a sensory panel. Of these, twenty-one were young men (M=19 years), ten were elder men (M=38 years), five were older men (M=55 years), five were young females (M=27 years), five were elder females (M=37 years), and two were older females (M=56 years). For the paired preference test, each member was given two canned samples, one with the essence and the other without it. They showed preference with a card.

RESULTS & DISCUSSION

The volatile compounds isolated from samples are listed in **Table 1**. The retention indices and concentration of them are also shown in this table. The concentration of limonene in the fresh juice sacs was 482.6 ppb, while that in the canned Satsuma mandarin stored for one month at room temperature was 401.9 ppb. The limonene concentration of the canned Satsuma mandarin with the essence stored for one month at room temperature, the one stored for four months at 37℃ and the another one with the essence stored for four months at 37℃ were 26.5 ppm, 416.9 ppb and 13.3 ppm, respectively. In the case of those stored for four months at 37℃, the concentration of limonene of the canned Satsuma mandarin wih the essence was thirty-two times as high as that of the control. In the canned Satsuma mandarin, the smell of limonene was not strong. The linalool concentration of the fresh juice sacs was 16.1 ppb, while the canned Satsuma mandarin stored for one month at room temperature was 9.9 ppb. The linalool concentration of the canned Satsuma mandarin with the essence stored for one month at room temperature was 2.8 ppm. The linalool was not detected in the canned Satsuma mandarin stored for four months at 37℃. The linalool concentration of the canned Satsuma mandarin with the essence stored for four months at 37℃ was 168.9 ppb. This indicates that the essence can maintain the levels of linalool even in the canned Satsuma mandarin stored for four months at 37℃. Furthermore, myrcene, *p*-cymene, δ-elemene, β-elemene, β-caryophyllene, α-caryophyllene, germacrene D, α-farnesene, (*E*)-carveol and hexanal were left more abundantly in the canned Satsuma mandarin with the essence. Linalool and hexanal in the canned Satsuma mandarin with the essence were not lost during the course of storage. The remaining of hexanal caused freshness to the canned Satsuma mandarin. α-pinene, 1, 8-cineol, citronellol, nerol, (*Z*)-carveol, β-elemol, (*Z*)-citral, (*E*)-citral and perillaldehyde did not originally exist in the juice sacs, but in the essencial oil. When the essence was added to the canned Satsuma mandarin, these terpenoids existed in the canned Satsuma mandarin stored for four months at 37℃ and gave the canned Satsuma mandarin much freshness. For example, odor description of α-pinene, citronellol and perillaldehyde were the ones of mandarin's peel, lemon and *Perilla frutescens* forma, respectively. Canned fruits were evaluated sensually. **Table 2** shows the result of the paired preference test.

The canned Satsuma mandarin with the essence was much more favored than the canned without it, significantly at the 1% level. Sixty-five percent of young men had a preference for the canned Satsuma mandarin with essence. Sixty percent of

Table 1 Volatile compounds of fresh juice sacs, the essences and the canned Satsuma mandarin (*Citrus unshiu* MARC. cv. Miyagawa-wase) which contained essence

			Concentration, $\mu g \cdot kg^{-1}$ [a]					
			Fresh	Essence	Canned products, Storage time [b]			
		K I			Room temp. 1month		37℃, 4months	
Peak No.	Compounds	(DB-Wax)	juice sacs	Satsuma mandarin	Without essence	With essence	Without essence	With essence
	Terpenoids							
4	α-Pinene	1020	-	145130	-	210.0	-	4.9
8	β-Pinene	1106	1.8	13539	1.1	8.5	-	-
9	Sabinene	1121[c]	-	60414	-	25.3	-	-
14	Myrcene	1163	3.2	365793	2.5	483.6	3.8	389.8
15	α-Terpinene	1179	-	-	1.1	N.D.	-	55.9
17	Limonene	1197	482.6	28217620	401.9	26534.4	416.9	13334.3
20	1, 8-Cineol	1211	-	N.D.	-	N.D.	-	26.4
22	γ-Terpinene	1246	27.5	18941	23.5	98.3	14.8	74.8
25	*p*-Cymene	1271	11.6	14834	11.9	44.8	12.2	47.5
26	α-Terpinolene	1284	0.9	8715	1.6	11.7	2.5	118.8
39	δ-Elemene	1477[c]	8.2	14552	1.0	68.2	-	39.2
41	Copaene	1501[c]	-	3746	-	16.3	-	14.5
43	β-Cubebene	1547[c]	-	7719	-	5.4	-	-
47	β-Elemene	1600[c]	4.6	18777	-	24.6	-	12.0
48	β-Caryophyllene	1606	1.7	16395	1.8	58.8	-	18.4
53	α-Caryophyllene	1680	1.5	4462	0.5	13.7	-	10.7
60	GermacreneD	1722[c]	7.0	27330	4.7	39.0	Tr	7.1
65	α-Farnesene	1754[c]	Tr	15565	1.2	26.2	Tr	32.5
68	γ-Cadinene	1768	11.6	11105	1.8	37.8	-	N.D.
44	Linalool	1552	16.1	1980700	9.9	2832.0	-	168.9
49	Terpinen-4-ol	1611	4.0	46240	1.8	200.6	-	107.5
50	β-Terpineol	1640	-	-	-	-	-	183.8
58	α-Terpineol	1707	9.1	397286	11.2	1045.6	41.1	2640.1
70	Citronellol	1772	-	61985	-	100.9	-	22.8
73	Nerol	1808	-	56392	-	95.3	-	12.2
74	(*E*)-Carveol	1845	6.7	46936	12.3	82.0	13.1	37.5
75	Geraniol	1855	-	73001	-	147.9	-	40.4
77	(*Z*)-Carveol	1876	-	17136	-	30.9	-	16.6
83	β-Elemol	2090[c]	-	67454	-	76.7	-	42.4
40	Citronellal	1483	-	76316	-	0.9	-	-
55	(*Z*)-Citral	1690	-	242377	-	21.0	-	4.5
63	(*E*)-Citral	1740	-	399327	-	70.1	-	9.8
72	Perillaldehyde	1797	-	113876	-	168.6	-	60.8
52	Citronellyl acetate	1666	-	22657	-	42.0	-	39.5
67	Gerany acetate	1762	Tr	27128	-	59.7	-	15.8
57	UK(M+=204)	1702	2.2	19382	3.4	28.3	Tr	25.0
61	UK(M+=204)	1731	86.7	38845	-	299.6	-	393.1
62	UK(M+=204)	1737	2.3	38543	-	223.1	-	25.0
64	UK(M+=204)	1747	-	78690	-	151.9	-	93.4
71	UK(M+=204)	1776	3.0	21203	3.7	31.1	-	21.7
			692.3	32790111	496.9	33414.8	504.4	18147.6
	Alcohols							
2	Ethanol	937	N.D.	19760	2.8	15.0	N.D.	19.4
5	2-Methyl-3-buten-2-ol	1044	15.7	-	47.1	67.9	72.6	84.1
7	2-Methyl-1-propanol	1096	4.5	-	9.2	11.1	14.1	15.3
12	1-Butanol	1148	Tr	-	1.2	-	4.8	1.0
13	1-Penten-3-ol	1162	5.4	-	4.9	4.4	6.6	6.2
16	3-Penten-2-ol	1182	-	-	-	-	5.6	7.7
18	2-Methyl-1-butanol	1210	13.4	N.D.	16.0	N.D.	17.2	N.D.
19	3-Methyl-1-butanol	1211	53.4	N.D.	64.1	N.D.	68.6	N.D.
23	1-Pentanol	1255	1.3	-	2.0	-	3.4	-
30	(*Z*)-2-Penten-1-ol	1325	2.5	-	4.0	5.5	3.7	3.0
31	3-Methyl-2-buten-1-ol	1326	7.6	-	12.7	16.6	14.5	18.3
32	1-Hexanol	1358	4.3	26606	3.9	49.0	3.7	44.4
33	(*Z*)-3-Hexen-1-ol	1389	12.8	64061	14.5	115.6	12.1	84.1

Table 1 continued

36	1-Heptanol	1461	-	2821	-	7.2	-	7.3
45	1-Octanol	1563	-	108905	1.1	177.3	-	167.9
69	1-Decanol	1769	-	-	-	-	-	157.6
85	Perilly alcohol	2018	-	8584	-	15.2	-	55.7
86	(*E*)-Nerolidol	2046	-	7484	-	16.6	-	6.2
			120.9	238221	183.5	501.4	226.9	678.2
	Aldehydes							
6	Hexanal	1082	3.2	18676	-	54.7	-	22.1
10	(*E*)-2-Pentenal	1129	1.3	-	1.0	1.1	-	-
11	(*Z*)-3-Hexenal	1143	2.8	-	-	-	-	-
21	(*E*)-2-Hexenal	1219	2.3	N.D.	3.1	N.D.	-	-
28	Octanal	1291	-	211858	-	554.6	-	132.6
34	Nonanal	1399	0.7	73736	-	172.4	-	39.1
37	Furfural	1466	4.7	-	22.9	29.5	1054.0	1041.8
42	Decanal	1503	-	581275	-	964.7	-	287.3
46	5-Methyl-2-furfural	1578	-	-	-	-	5.7	6.9
51	(*E*)-2-Decenal	1649	-	3415	-	8.3	-	-
59	Dodecanal	1716	-	78913	-	156.1	-	73.8
			15.0	967873	27.0	1941.4	1059.7	1603.6
	Paraffin Wax							
78	Nonadecane	1900	1.4	-	1.3	4.8	-	-
80	Eicosane	2000	19.0	-	13.7	17.2	12.7	14.5
82	Hydrocarbon	2051	33.1	-	23.7	21.9	17.8	17.9
84	Heneicosane	2100	141.9	-	90.6	108.4	103.0	100.8
87	Hydrocarbon	2149	29.8	-	18.9	23.5	20.4	25.6
88	Hydrocarbon	2164	26.4	-	16.7	29.1	13.3	22.9
90	Docosane	2200	133.9	-	83.0	110.9	98.0	80.4
93	Hydrocarbon	2253	413.7	-	260.6	299.4	249.8	287.6
95	Tricosane	2300	496.8	-	292.0	361.6	278.3	329.5
96	Hydrocarbon	2323	48.6	-	30.4	27.7	29.8	22.1
97	Hydrocarbon	2349	30.7	-	19.5	24.2	21.4	17.0
98	Hydrocarbon	2369	203.1	-	127.3	138.3	137.4	144.8
99	Tetracosane	2400	75.5	-	44.6	60.4	60.5	54.8
100	Hydrocarbon	2449	67.3	-	39.6	46.5	49.7	47.3
101	Pentacosane	2500	103.6	-	57.5	76.4	75.2	80.6
			1824.8	0	1119.4	1350.3	1167.3	1245.8
	Miscellaneous							
1	Acetic acid ethyl ester	885	-	-	-	-	62.7	84.1
3	Chloroform	1018	6.6	-	1.4	Tr	2.2	Tr
24	Dihydro-2-methyl-3(2*H*)-furanone	1266	-	-	-	-	14.8	17.1
27	3-Hydroxy-2-butanone	1288	109.8	-	105.7	118.5	140.7	117.7
29	1-Hydroxy-2-propanone	1302	-	-	-	-	7.8	6.2
84	Octanoic acid	2067	-	-	-	-	2.9	32.0
			116.4	0	107.1	118.5	231.1	257.1
	Unknowns							
35	UK	1443	0.9	-	1.9	1.1	-	0.7
38	UK	1467	-	3973	-	-	-	-
54	UK	1685	-	6274	-	17.3	-	15.6
56	UK	1698	-	11871	-	22.1	-	9.0
76	UK	1866	-	23131	-	14.9	-	10.4
79	UK	1951	-	7150	-	10.0	-	Tr
81	UK	2006	-	14724	-	8.2	-	-
89	UK	2196	-	2929	-	5.9	-	4.6
91	UK	2204	-	3561	-	8.7	-	9.1
92	UK	2243	-	65072	-	81.4	-	37.6
94	UK	2266	16.6	4333	10.5	10.1	5.6	6.3
102	UK	2528	14.6	51327	10.2	40.7	11.5	15.8
			32.1	194345	22.6	220.4	17.1	109.1
			2801.5	34190550	1956.5	37868.3	3206.5	22041.4

[a], Concentrations were calculated from total ion intensity by internal standard method (I.S. = cyclohexanol) without response correction; [b], Concentrations based on the weight of canned vesicles;

[c], Sakamoto et al. (1997) (5);

Tr, Trace; −, Not detected.

Table 2 Preference of judges for the canned Satsuma mandarin without the essence* or the canned Satsuma mandarin with the essence* by the paired preference test

The Canned Satsuma mandarin	Panelists	
	Number	Percent
Without the essence	14	29.2
With the essence	34**	70.8
Total	48	100.0

* The cans were thermostated for four months at 37±2℃ for use for test.

** Significant difference at the 1% level.

elder men had a preference for it. All older men had a preference for it. Eighty percent of young females had a preference for it. Eighty percent of elder females had a preference for it. All older females had a preference for it. The number of panelists preferring the canned Satsuma mandarin with the essence was significantly higher than that of panelists preferring the canned Satsuma mandarin without the essence.

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