Volatile Flavor Compounds of Sweetened Condensed Milk

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ABSTRACT: The volatile compounds of sweetened condensed milk (SCM) were investigated to explain their contribution to SCM flavor. Commercially processed SCM was diluted with water and the volatiles were isolated by simultaneous steam distillation-extraction under reduced pressure. Commercial liquid milk was used for comparison. The odor concentrate was analyzed by GC and GC-MS, and then fractionated by silica gel TLC and preparative GC to determine the contributors to SCM flavor. Major volatile compounds were 10 fatty acids, 14 lactones, 10 ketones, 13 hydrocarbons, 8 alcohols, 4 aldehydes, and 8 miscellaneous compounds. δ-Decalactone and δ-dodecalactone were the principal contributors to SCM flavor although the other lactones may contribute as well.

Key Words: volatiles, flavor, aroma, sweetened condensed milk, milk products

Introduction

SWEETENED CONDENSED MILK (SCM) Is essentially concentrated liquid milk preserved by the addition of a high concentration of sugar. The high osmotic pressure of SCM inhibits the growth of most spoilage organisms and provides long shelf life without refrigeration. Nowadays, SCM is used not only as a spread or sweetening but also as a material for various food products to improve their flavor, taste, and mouthfeel. It is interesting to note that the characteristic sweet and milky flavor of SCM develops during manufacturing.

To date, no information is available on the flavor of SCM, the most important aspect of its quality, although much work has been carried out on the flavor of liquid milk and dairy products (Badings and Neeter 1980; Rerkrai and others 1987; Badings 1991; Gaafar 1991; Shiratsuchi and others 1994a, 1994b, 1995; Stevenson and others 1996). We have carried out, therefore, a study on the isolation and identification of volatiles in SCM to determine the contributors to SCM flavor.

Materials and Methods

Materials Used

Commercially processed SCM was obtained from Meiji Milk Products Co., Ltd. (Tokyo, Japan), with a composition as shown in Table 1. In addition, SCM samples were prepared in our laboratory. To carry out this evaluation for SCM flavor, recombined sweetened condensed milk with reduced characteristic flavor of SCM was made from skim milk powder, sucrose, and water (Newstead 1982). Liquid milk was purchased locally. Silica gel 60 F254 plates for thin-layer chromatography (TLC) of the odor concentrates were obtained from Merck (Darmstadt, Germany). Diethyl ether and anhydrous sodium sulfate were obtained from Nakarai Tesque Inc. (Kyoto, Japan), and 2-ethylhexyl acetate was obtained from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). δ-decalactone and δ-dodecalactone were received from Ogawa Perfumery Co. Ltd. (Tokyo, Japan).

Table 1—Composition of the sweetened condensed milk (%)

Sucrose	44.2
Water	25.5
Lactose	12.2
Fat	8.3
Protein	7.9
Ash	1.9

Isolation of volatile flavor compounds

Canned SCM (379 g) and 800 mL deionized water were placed in a 2000-mL round-bottom flask. Volatiles were separated with 80 mL diethyl ether from the diluted SCM solution by simultaneous distillation-extraction under reduced pressure (approximately 80 mmHg) for 1 h, using a modified Likens-Nickerson apparatus. After addition of 20 μL of 1% diethyl ether solution of 2-ethylhexyl acetate, the extract was dried over anhydrous sodium sulfate for 6 h and concentrated to about 100 μL. Twenty-five samples of the SCM were successively treated. The concentrates were combined and further concentrated to about 500 μL. The odor concentrate from liquid milk (10 L) was prepared in the same way as the isolation of flavor volatiles from the SCM. The odor concentrate from 10 kg of SCM, which had a typical SCM odor (sweet and milky), was fractionated by silica gel TLC (the solvent was diethyl ether/n-pentane, 20:80). The 2 polar fractions with sweet and milky odor, which seemed to contribute directly to the characteristic flavor of SCM, were eluted with diethyl ether (30 mL) from the silica gel support scraped from the TLC plate and then concentrated to about 100 μL.

Capillary gas chromatography (GC)

Capillary GC analysis was carried out on a Hewlett-Packard Model 5890A gas chromatograph equipped with a flame ionization detector (FID) and connected to a Shimadzu Chromatopak C-R5A integrator. Separation was achieved on a 60 m × 0.25 mm i.d. fused silica capillary column, coated with cross-linked polyethylene glycol 20M, film thickness 0.25 μm (DB-Wax; J&W Scientific, Folsom, Calif., U.S.A.). The oven temperature was programmed from 50 to 230 °C at 2 °C / min (60-min hold). The injector and detector temperatures were 230 and 250 °C, respectively. The helium carrier gas flow rate was 25 cm/s with an injection splitter at a split ratio of 25:1. Retention indices were estimated in accordance with a modified Kovats method (Van den Dool and Kratz 1963).

Capillary gas chromatography-mass spectrometry (GC-MS)

Electron impact mass spectrometric data were collected on a JEOL Auto-

mass 50 mass spectrometer interfaced to a Hewlett-Packard 5890 Series II gas chromatograph. The column and chromatographic conditions were the same as described for the GC analysis. The mass spectrometer was operated at an ionization voltage of 70 V and an ion source temperature of 200 °C. The mass spectra of the unknown compounds were compared with those in the Wiley/NBS Registry of Mass Spectral Data (1989).

Preparative GC and sniffing

The odor extracts from 2 polar fractions with sweet and milky odor were further fractionated by preparative GC (Shimoda and others 1993) to detect contributors to the odor attributes.

Results and Discussion

THE COMPOUNDS IDENTIFIED INCLUDED 10 fatty acids, 14 lactones, 10 ketones, 13 hydrocarbons, 8 alcohols, 4 aldehydes, and 8 miscellaneous compounds (Table 2). Total area of 67 peaks which were identified definitely by retention indices and mass spectra or tentatively by only mass spectra represented about 94% of the chromatogram peak surface area (excluding solvent and internal standard peak). Among fatty acids, even-carbon-numbered saturated fatty acids, which have buttery, milky, creamy or waxy odors, were predominant. These compounds were also found to be important in the silica gel TLC fraction of skim milk flavor compounds (Shiratsuchi and others 1995). It was shown that a pronounced amount of lactones was included. Major components were δ-decalactone, γ- and δ-dodecalactone, and δ-tetradecalactone. These compounds have milky, buttery, or creamy odors, and hence, are added to some margarines to simulate butter flavor (Kinsella and others 1967). It was reported that γ-lactones were produced from 4-hydroxy fatty acids by heating and δ-lactones were produced from 5-hydroxy fatty acids (Forss 1979). Methyl ketones are a notable feature in the flavor of milk and milk products. Among the ketones, odd-carbon-numbered ones, that is, 2-heptanone, 2-nonanone, 2-undecanone and 2-tridecanone were principal components. Langler and Day (1965) found that flavor potency varied with carbon-chain length and 2-heptanone had the lowest flavor threshold value (700 ppb). The content of methyl ketones in the SCM was quite low, far below the flavor thresholds in milk. Volatile compounds of other chemical classes were present

Table 2–Volatile flavor compounds identified in sweetened condensed milk

Peak		Kovats index[a]	ppb
	(A) Fatty acids		
17	acetic acid	1452	2.8
32	hexanoic acid	1852	1.0
43	octanoic acid	2069	10.0
49	decanoic acid	2288	79.5
51	10-undecenoic acid[b]	2358	1.3
57	dodecanoic acid	2503	182.0
63	tetradecanoic acid	2716	62.7
65	tetradecenoic acid	2763	14.1
67	pentadecanoic acid	2819	8.2
69	hexadecanoic acid	2928	59.5
	(B) Lactones		
36	δ-heptalactone	1976	0.6
38	δ-octalactone	1999	1.9
45	γ-decalactone	2185	1.1
47	δ-decalactone	2229	62.6
50	δ-undecalactone	2345	2.2
52	γ-dodecalactone	2397	14.0
54	γ-dodecenolactone[b]	2427	5.8
55	δ-dodecalactone	2466	54.7
56	γ-tridecalactone[b]	2488	3.9
59	δ-tridecalactone[b]	2565	2.0
61	γ-tetradecalactone[b]	2628	4.3
62	δ-tetradecalactone[b]	2701	24.1
66	δ-pentadecalactone[b]	2802	6.2
68	δ-hexadecalactone[b]	2912	4.0
	(C) Ketones		
1	2-pentanone	996	1.8
4	2-heptanone	1183	25.1
16	2-nonanone	1389	7.1
19	2-decanone	1496	2.2
22	2-undecanone[b]	1598	15.3
25	2-dodecanone	1692	1.2
31	2-tridecanone[b]	1816	11.7
33	2,3,4-trimethylacetophenone[b]	1859	1.1
34	2-tetradecanone	1941	0.5
42	2-pentadecanone[b]	2041	1.5
	(D) Hydrocarbons		
3	toluene	1039	0.7
5	propylbenzene	1203	1.8
6	1-ethyl-4-methylbenzene	1216	3.2
7	1-ethyl-3-methylbenzene	1219	8.5
8	1,3,5-trimethylbenzene	1237	4.1
9	1-ethyl-2-methylbenzene	1254	3.2
10	1,2,4-trimethylbenzene	1275	18.6
11	1,3-diethylbenzene	1296	1.7
12	tridecane	1300	1.1
13	1,2,3-trimethylbenzene	1329	3.7
14	1,1-dimethylethylbenzene[b]	1359	1.5
26	heptadecane	1700	5.2
28	octadecane	1800	2.5
	(E) Alcohol		
2	2-methyl-3-buten-2-ol[b]	1035	0.8
18	2-ethyl-1-hexanol[b]	1492	1.8
23	2-furanmethanol	1655	0.6
29	2-methyl-1-decanol[b]	1803	16.0
46	tetradecanol	2205	1.2
58	heptadecanol	2524	1.2
60	octadecanol	2626	1.1
	(F) Aldehydes		
15	nonanal	1389	11.7
20	benzaldehyde	1531	6.9
21	(*E*)-2-nonenal	1557	1.0
40	2-tetradecenal[b]	2012	1.0
	(G) Miscellaneous Compounds		
24	cyclohexyl isothiocyanate[b]	1667	3.9
27	N,N-dibutyl acetamide	1805	5.8
35	benzothiazole	1968	2.1
39	phenol	2006	1.3
41	methyl tetradecanoate	2028	9.5
44	1-methoxynaphthalene[b]	2135	2.6
48	methyl hexanoate	2251	1.3
64	dibutyl phthalate	2726	26.4

[a] Modified Kovats indices calculated for DB-Wax capillary column on the GC system.
[b] Tentative identification by mass spectrum alone.

in extremely low concentrations. Therefore, they could play only a secondary role in SCM flavor.

The absolute contents of classes of the volatile compounds from the SCM and commercial liquid milk are shown in Figure 1. A comparison of the levels of each class showed that all of the levels in the SCM were much higher than in the liquid milk, that is, the class of fatty acids was 8.4 times, lactone 35.3 times, ketones 2.2 times, hydrocarbons 5.4 times, alcohols 20.7 times, and aldehydes 12.1 times higher in SCM than in liquid milk. There were large differences in the concentration of flavor compounds between SCM and liquid milk. The difference in the lactones was most noteworthy. Such a striking difference in the concentrations might result from decomposition of their precursors or the release of bound volatiles during the manufacturing processes of SCM.

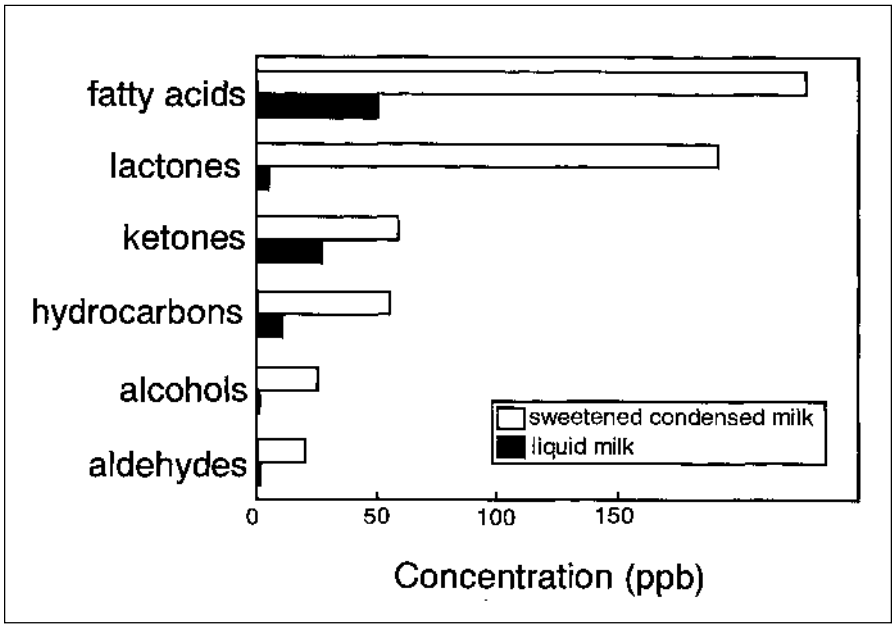
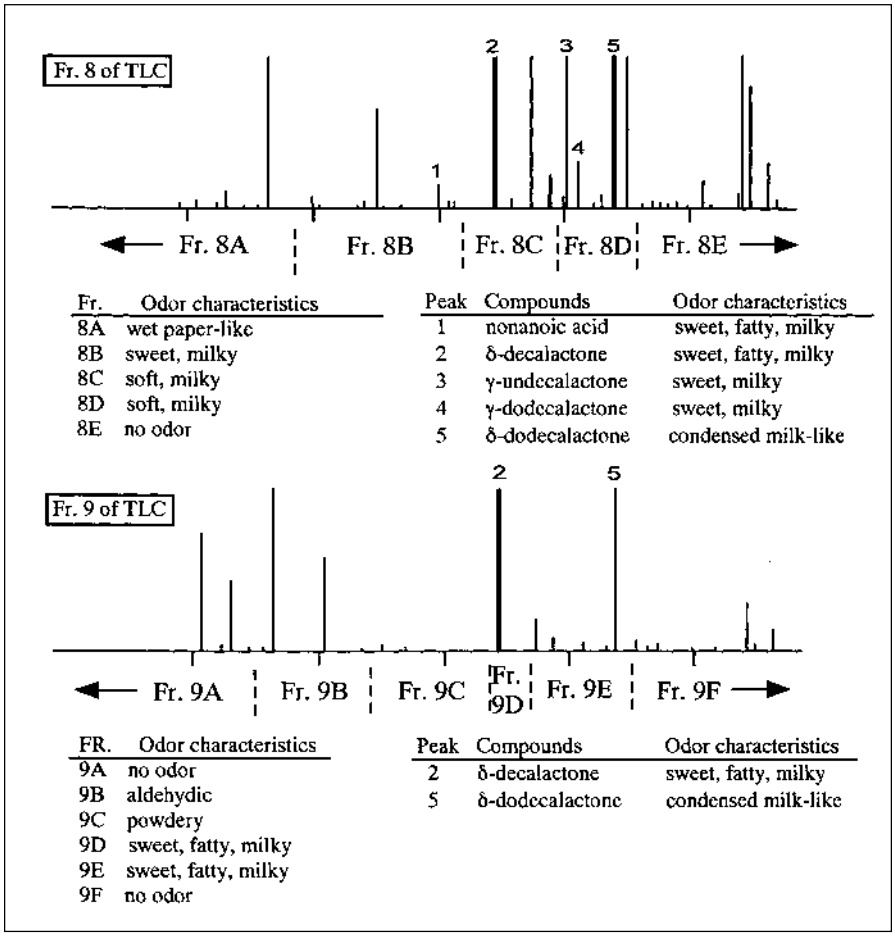


Figure 1—Levels of volatile compounds grouped according to chemical class in sweetened condensed milk and liquid milk.



Fr.	Odor characteristics
8A	wet paper-like
8B	sweet, milky
8C	soft, milky
8D	soft, milky
8E	no odor

Peak	Compounds	Odor characteristics
1	nonanoic acid	sweet, fatty, milky
2	δ-decalactone	sweet, fatty, milky
3	γ-undecalactone	sweet, milky
4	γ-dodecalactone	sweet, milky
5	δ-dodecalactone	condensed milk-like

FR.	Odor characteristics
9A	no odor
9B	aldehydic
9C	powdery
9D	sweet, fatty, milky
9E	sweet, fatty, milky
9F	no odor

Peak	Compounds	Odor characteristics
2	δ-decalactone	sweet, fatty, milky
5	δ-dodecalactone	condensed milk-like

Figure 2—Sniffing of the fractions obtained by preparative gas chromatography on fractions 8 and 9 from the thin-layer chromatogram.

To specify the compounds that directly contribute to the flavor of SCM, a fractionation of odor concentrate was carried out by thin-layer chromatography. Among 9 fractions separated, fractions 8 and 9 had sweet and milky odors, reminiscent of the flavor of SCM. It is possible that contributors to SCM flavor are included in these fractions. Therefore, fractions 8 and 9 were each separated into several portions by preparative GC (Figure 2). As shown in Figure 2, fractions 8B, 8C, and 8D had sweetened condensed milk-like odors. Each peak of 8B, 8C, and 8D was further separated and their odors were sniffed during elution. Peak 1, nonanoic acid, had a sweet, fatty, and milky odor; peak 2, δ-decalactone, a sweet, fatty, milky odor; peak 3, γ-undecalactone, a sweet and milky odor; peak 4, γ-dodecalactone, a sweet and milky odor; and peak 5, δ-dodecalactone, a condensed milk-like odor. Fractions 9D and 9E had sweet, fatty and milky odor as shown in Figure 2. Judging from the sniffing and their quantitative values, the most important contributors seemed to be δ-decalactone and δ-dodecalactone. Therefore, after addition of authentic compounds of δ-decalactone and δ-dodecalactone to a laboratory-made SCM sample the flavor was evaluated organoleptically by a triangle test with a 10-member panel. Both the lactones were added in the same and double concentrations as in the commercial SCM product (Table 3). It was confirmed that the sweet and milky flavor of sample A was more intense than that of the control ($p < 0.01$), and $p < 0.001$ for sample B. These results indicated that δ-decalactone and δ-dodecalactone were the principal compounds contributing to the flavor of SCM, although the other lactones are probably also contributors.

Table 3–Composition of the sweetened condensed milk for addition evaluation.

Ingredient	Control	Sample A	Sample B
Skim milk powder (%)	24.0	24.0	24.0
Sucrose (%)	48.0	48.0	48.0
Water (%)	28.0	28.0	28.0
δ-decalactone(ppb)	0.0	62.6	125.2
δ-dodecalactone (ppb)	0.0	54.7	109.4

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