J. Korean Soc. Food Nutr.
21 (6), 731 ~ 737 (1992)

한국영양식량학회지

Origin of Flavor Compounds in Canned Tuna and Their Relation to Quality

Mu-Nam Kim[†] **and R. C. Lindsay***

Dept. of Food and Nutrition, Pusan Women's University, Pusan 607-737, Korea
*Dept. of Food Science, University of Wisconsin-Madison, Madison, WI 53706, USA

Abstract

The specific attributes of aroma quality of canned tuna meat were investigated before and during refrigerated storage. Fresh, cooked tuna, beefy and meaty flavor notes of canned tuna meat were changed to card-boardy (1 week storage), oxidized fat-like (2 weeks storage), fatty acid-like and heavy oxidized fat-like (3 weeks storage), and then moldy and painty (4 weeks storage) flavor notes during storage in refrigerator at 4° C. More than 126 peaks of volatile compounds collected from canned tuna meat were separated on Carbowax 20M capillary column of gas chromatographic analysis. Of the peaks, 54 compounds were identified by mass spectral data, matching I_E values, and sniffing the effluent of each peak from GC detector. The contents of many low molecular weight compounds eluted with early retention times were decreased, whereas some other new compounds eluted with longer retention time were formed during storage. The compounds increased up to 3 weeks of storage and then decreased at extended storage time (4 weeks) were 1-penten-3-ol, 3-penten-2-ol, heptanal, limonene, 1-pentanol, octanal, 1-hexanol, nonanal, 2-octanone, 2-nonanone, 1-heptanol, benzaldehyde and some methyl substituted benzenes. *p*-Thiocresol, 2-chlorophenol, 1, 2-dichlorobenzene, dipropyl disulfide, 2-isobutyl-4, 5-dimethylthiazole, diethyltrisulfide, and 2-heptylthiophene were formed after 4 weeks of storage, but not detected in fresh canned tuna. Therefore, these compounds could be used as indicators for the quality changes during refrigerated storage.

Key words : volatile compounds, canned tuna, refrigerated storage

INTRODUCTION

Canned tuna has relatively a long shelf life at room temperature as well as refrigerated temperature, if not opened. Sometimes, consumers store the left-over canned tuna in a refrigerator after opening the can. Frequently, the quality of canned tuna after openning the can during storage is determined by smelling the top note. Thus, the flavor and related flavor compounds should be an important indicators to detect the freshness of canned tuna before the microbial deterioration occurs. As result, the olfactory judgement of odor has been and is still the main criterion. However, it is extremely difficult to qualify and quantify the characteristics of odors and uncertain to assess. The means of chemical analysis are believed to be the consistant indicators of changes in flavor quality during storage. Many chemical tests have been proposed as indices of spoilage and quality[1,2]. Complicating factors affecting the flavor quality of canned tuna during storage have been discussed such as temperature, oxygen, and the types of microorganisms[3,4]. However, only limited information has been published concerning the changes of volatile flavor compounds in canned

---

[†] To whom all correspondence should be addressed

This study was supported by non directed research fund, Korea Research Foundation, 1988(Research fund number : 25505-714)

tuna meat and their affects to the quality during storage.

In the present study, we investigated the changes of volatile flavor compounds during storage at the refrigerated temperature (4° C) and the presence of oxygen(canned tuna spreaded on aluminum foil dish), which is the most common storage condition at home and restaurant.

MATERIALS AND METHODS

Materials

Canned tunas (Albacore ; *Thunnus alalunga*) filled with oil were obtained from commercial sources. Contents of the canned tuna were throughly mixed in a mortar, and then 20g of each mixed tuna sample was evenly spreaded on the aluminium foil dish at about 1cm thickness. The aluminium foil dishes containing the mixed tuna sample were stored in the temperature controlled refrigerator (4° C) for 4weeks. Each dish was removed from refrigerator every week for the analysis of volatile compounds and the sensory evaluation.

Methods

Volatile compounds of the mixed tuna was quantitatively analyzed according to the method developed by Olafsdottir *et al*5). Tuna sample (50g) containing internal standard (1 µg of 4-decanol in ethanol ; Aldrich Chemical Co., Milwaukee, WI) were blended with 250ml of saturated sodium chloride solution with a Waring Blendor (Hartford, CT) at high speed for 30s. After placing each of the slurries in a round bottom flask(500 ml), they were purged for 3 hrs with nitrogen(300ml/min) onto Tenax GC®(60 to 80mesh ; ENKA N.V. Holland). The purging was carried out at room temperature. Volatile compounds were eluted from the Tenax GC traps with redistilled diethyl ether into concentrate tube (Laboratory Research Company, Los Angeles, CA), and then extracts were concentrated under a stream of nitrogen to about 10µl for GC analysis.

Volatile flavor compounds in the diethyl ether concentrate (1 µl) were separated using a Carbowax 20M capillary column (60m × 0.32 mm, i.d., 0.25µm coating thickness ; J and W Scientific, Inc., Rancho Cordova, Cal) with a Varian model 3700 gas chromatograph (Palo Alto, CA) equipped with a flame ionization detector (temperature, 250° C ; hydrogen, 30ml/min ; air, 300 ml/min). Helium was used as carrier (2ml/min) and make-up gases (30ml/min). The oven temperature was programmed from 50° C to 250° C at 2° C/min, and the on-column injection system employed a temperature program from 50° C to 250° C at 100° C/min after injection. The identification of volatile compounds was carried out by GC retention indices (I_E) 6), aroma assessment of each peak from the effluent from the column end, and the mass spectral data of gas chromatography-mass spectrometry (GC - MS).

Aroma assessment for peaks was carried out by authors and others experienced in assessing aromas by sniffing the effluent carrier gas from the end of capillary column (Carbowax 20M) during GC analysis of the extract. Aromas were matched with GC peaks using timed notations marked on a stripchart recorder which was operated under conditions identical to analytical runs.

GC-MS was carried out with a Finnegan 4500GC - MS equipped with a Carbowax 20M capillary column with helium as a carrier gas (head pressure, 10psi ; split, 10ml/min ; sweep, 5ml/min). The same oven temperature profile described for the GC analysis was used.

RESULTS AND DISCUSSION

The specific attributes of aroma quality of canned tuna meat were investigated before and during storage. Fresh, cooked tuna, beefy and meaty flavor notes of canned tuna meat were changed to cardboardy (1 week storage), oxidized fat-like (2weeks storage), fatty acid-like and heavy oxidized fat-like (3weeks storage), and then moldy and painty (4 weeks storage) flavor notes during storage in refrigerator at 4° C (Table 1). More than 126 peaks of volatile compounds collected from canned tuna

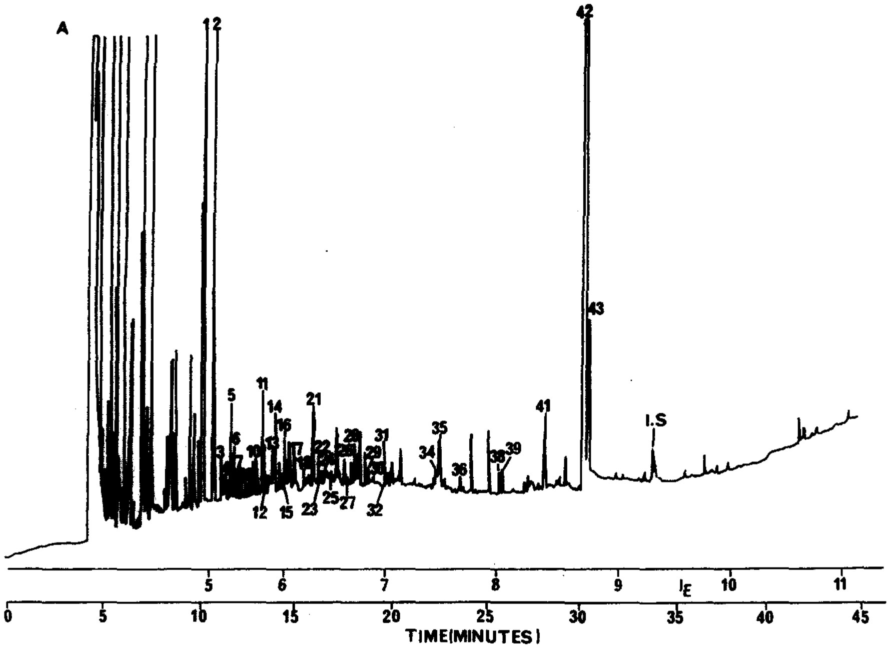
Table 1. Flavor description of canned tuna samples stored in refrigerator (4° C)

Storage time (week)	Flavor description
0	Fresh, cooked tuna, beefy, meaty
1	Beefy, meaty, slightly card-boardy cooked tuna
2	Card - boardy, oxidized - fat like
3	Butyric acid and other fatty acids, heavy oxidized - fat like
4	Strong butyric acid, card-boardy, moldy, painty

meat (Fig. 1) were separated on Carbowax 20M capillary column (60m × 0.32mm i. d.) of gas chromatographic analysis. Of the peaks, 54 compounds were identified by mass spectral data, matching I_E values, and sniffing the effluent of each peak from GC detector (Table 2). Saturated hydrocarbones, unsaturated hydrocarbones including terpenes, and aromatic hydrocarbones, alcohols, aldehydes, ketones, esters, pyrazines, sulfur compounds, and phenols were the classes of compounds identified from fresh canned tuna meat and stored canned tuna meat. Early studies employed Tenax trap methods[7-14] for the analysis of fish volatile compounds showed the many of the compounds identified from tuna meat also present in other fish meat and play an important role for the general fish flavor. Traditionally, amines have been included a major characterizing group of flavor compounds in most of the fish volatiles[8,15], however they were not identified from canned tuna meat used in this study. As shown in chromatogram (Fig. 1), the contents of many low molecular weight compounds eluted with early retention times were decreased, whereas some other new compounds eluted with longer retention time were formed during storage. The decrease in concentrations of the volatile compounds may due to the loss of volatiles and / or their intermediary roles ; leading to the formation of other end products during storage. The increase in high molecular weight compounds might be related to bacterial action on canned tuna meat during storage. Bacterial digestion of the meat tissue leads to formation of extensive number of volatile compounds.

Although the concentrations of the most of volatile compounds were varied during storage, the volatile compounds were classified as three categories of the compounds decreased, increased, and not changed in the concentration during storage. The concentration of 1-penten-3-ol was decreased up to 2weeks storage time and then slightly increased after 3week storage(2.68ppm), and decreased again after 4week storage (0.02) (Table 2). 1-Penten-3-ol has been found in raw tuna[16] and reported that the compound decreased as the spoilage time was extended. This compound has been used for the development of quality index of raw tuna[16]. The proposed reason for this may be related to a greater degradation rate by bacteria as opposed to generation rate by oxidation of unsaturated fatty acids. As the same classes of compounds with 1-penten-3-ol, 3-penten-2-ol, heptanal, limonene, 1-pentanol, octanal, 1-hexanol, nonanal, 2-octanone, 2-nonanone, 1-heptanol, benzaldehyde and some methyl substituted benzenes were obviously decreased as the extended storage time (Table 2). 1-Penten-3-ol and pentanol found in fresh[17] and in oxidized whitefishes[9]. Limonene (peak 9, Fig. 1) has been identified as a major component in the volatiles of Citrus fruits[18] and aroma characteristic of the authentic compound is lemon-like flavor. Limonene has been identified in oxidized whitefish, but not in fresh one[9] indicating that this compound may be the oxidation product of fish. The compounds having characteristic mushroom-like aromas (2 - octanone, peak 24, Fig. 1) also decreased as the storage time is extended. Hexanol (peak 32, Fig. 1) contributes green, plant - like aromas and nonanal (peak 35, Fig. 1) contributes cucumber and melon - like aromas in fish products.

p-Thiocresol, 2-chlorophenol, and 1, 2-dichlorobenzene were not detected in fresh canned tuna sample and the sample stored up to 3weeks, but detected in the tuna sample stored for 4weeks. These aromatic compounds have decomposition aromas of fish[11] and contribute to the sensory quality deterioration. Among sulfur-containing compounds, 3-thiophene seemed to contribute partly to meaty flavor of fresh canned tuna, but others including dipropyl disulfide, 2-isobutyl-4, 5-dimethylthiazole, diethyltrisulfide, and 2-heptylthiophene contribute to the deteriorated tuna meat


A
1
2
5
11
14
16
21
3
6
7
10
13
17
19
22
28
31
29
12
15
23
25
27
32
34
35
36
38
39
41
42
43
I.S
5
6
7
8
9
I_E
10
11
0
5
10
15
20
25
30
35
40
45
TIME(MINUTES)

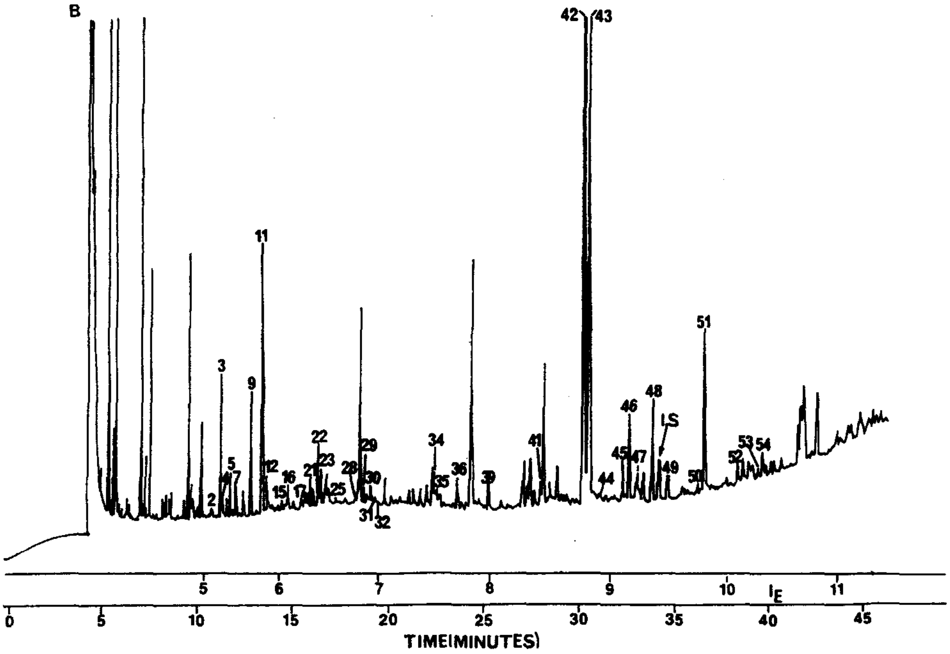

B
42
43
11
3
9
2
4
5
7
12
15
16
17
21
22
23
25
28
29
30
31
32
34
35
36
39
41
44
45
46
47
48
I.S
49
50
51
52
53
54
5
6
7
8
9
10
I_E
11
0
5
10
15
20
25
30
35
40
45
TIME(MINUTES)

Table 2. Concentrations of volatile compounds isolated and identified from canned tuna stored (0, 1, 2, 3, 4 weeks) in refrigerator (4° C)

Peak No.	Compounds	I_E[a]	Storage time (week)				
			0	1	2	3	4
			concentration (ng/g)				
1	1,4-Dimethyl benzene	5.0	4,850	2,960	3,103	4,130	
2	1-Penten-3-ol	5.14	1,760	240	1,527	2,680	20
3	Myrcene	5.26	230	100	110	120	110
4	3-Penten-2-ol	5.30	170			70	20
5	Pyridine	5.38	840	310	427	730	40
6	2-Heptanone	5.42	120		110	100	
7	Heptanal	5.45	220			80	40
8	2,4,5-Trimethyl oxazole	5.50	100				
9	Limonene	5.60	120	140	245	1,070	110
10	3-Methyl butanol	5.73	220		132	90	
11	Dodecane	5.79	720	330	420	550	250
12	1-Ethyl-3-methyl benzene	5.86	340	160	190	210	60
13	n-Amyl alcohol	5.92	320	180	130	140	
14	2-Pentylfuran	5.94	230		210	180	
15	1, 3, 5-Trimethyl benzene	6.05	350	120	170	320	20
16	1-Pentanol	6.10	520	310	320	300	50
17	Styrene	6.24	170	270	240	190	20
18	2,4-Nonadiene	6.26	120			110	
19	Hexylacetate	6.28	130	100	90	80	20
20	3-Thiophene	6.30	110		120	110	30
21	Hexyl acetate	6.33	650		630	510	30
22	A methyl pyrazine	6.39	350	360	270		20
23	1, 2, 4-Trimethyl benzene	6.43	210	250	260	290	50
24	2-Octanone	6.46	140	150	130	90	
25	Octanal	6.53	360	120	190	310	40
26	Butenyl cyclohexene	6.65	190	140	130	120	
27	Cyclopentanol	6.68	170			150	
28	Tridecane	6.76	150	210			20
29	1-Ethyl-2,3-dimethyl benzene	6.89	170	140	180	230	30
30	1, 2, 3-Trimethyl benzene	6.94	140	130	120	130	40
31	1-Methylpropyl benzene	6.98	140	120	130	120	20
32	Hexanol	7.06	120	100	110	160	20
33	Dipropyl disulfide	7.38					20
34	2-Nonanone	7.50	140		180	100	50
35	Nonanal	7.53	450	209	140	150	40
36	Tetramethylbenzene	7.71	120				40
37	1, 2-Dichlorobenzene	8.00					160
38	1-Octen-3-ol	8.06	110	260	180	100	
39	1-Heptanol	8.08	160	170	190	200	20
40	1, 2, 4, 5-Tetramethyl benzene	8.41				120	
41	3, 5, 5-Trimethyl-1-hexanol	8.44	460	400	370	300	40
42	Benzaldehyde	8.77	12,380	12,200	13,240	14,180	7,950
43	Pentadecane	8.79	890	1,420	1,520	830	2,700
44	2-Isobutyl-4,5-dimethylthiazole	8.93					20
45	Diethyltrisulfide	9.11					30
46	t-3-Octenol	9.17					100
47	Isoamyl heptanoate	9.24					80
48	3, 5-Octadiene-2-one	9.36					150
49	Octanol	9.49					30
50	p-Thiocresol	9.75					20
51	2-Chlorophenol	9.81					220
52	Furanmethanol	10.09					30
53	2-Heptylthiophene	10.23					20
54	3, 5-Octadien-2-ol	10.32					40

[a] Reference 6)

flavor (Table 2) due to formation after 4 weeks of storage. However, 2-methyl-3-furanthiol that has been reported beefy aroma compound as in the steam distillate of canned tuna[19], was not found in any of the samples analyzed in this study. A methylpyrazine (peak 22) and 2 ,4 ,5 - trimethyloxazole - (peak 8) were found in fresh canned tuna meat, but disappeared during storage, and thus, they contribute to the brothy meat flavor note of fresh canned tuna meat. The concentration of benzaldehyde (peak 42) was decreased, while the concentration of pentadecane (peak 43) was slightly increased after 4 weeks of storage (Table 2). Benzaldehyde and pentadecane have historically been found in fish volatiles[7,9~11,14], but their role for the fish flavor have not been clearly understood. As considered the flavor characteristics of their authentic compounds, the sweet, cherry-like flavor note contributed by benzaldehyde may decrease and petroleum-like flavor note by pentadecane may increase in tuna meat after 4 weeks of storage.

In summary, of the peaks(126) separated by gas chromatographic analysis (Carbowax 20M capillary column) from canned tuna meat volatiles, 54 compounds were identified. The contents of many low molecular weight compounds eluted with early retention times were decreased, whereas some other new compounds eluted with longer retention time were formed during storage. The compounds increased up to 3 weeks of storage and then decreased at extended storage time (4 weeks) were 1-penten-3 - ol, 3-penten-2-ol, heptanal, limonene, 1-pentanol, octanal, 1-hexanol, nonanal, 2-octanone, 2-nonanone, 1-heptanol, benzaldehyde and some methyl substituted benzenes. *p*-Thiocresol, 2-chlorophenol, 1,2-dichlorobenzene, dipropyl disulfide, 2-isobutyl-4,5-dimethylthiazole, diethyltrisulfide, and 2-heptylthiophene were formed after 4 weeks of storage, but not detected in fresh canned tuna. And these volatile flavor compounds could be used as quality indices of canned tuna meat.

REFERENCES

1. Lerke, P. A. and Huck, R. W. : Objective determination of canned tuna quality identification of ethanol as a potentially useful index. *J. Food Sci.*, **42**, 755 (1977)
2. Khayat, A. : Correlation of off-odor scores of canned tuna with gas chromatographic data. *J. Food Sci.*, **44**, 37 (1979)
3. Oliveira, L., Madi, L., Sarantopoulos, C., Mori, E. and Shirose, I. : Processed tuna fish : potentially for an alternative package. *Bol. Inst. Technol. Aliment* (Campina, Braz), **23**, 117 (1986)
4. Pirazzoli, P., Ambroggi, F. and Incerti, I. : Canned tuna in oil : changes in composition as related to cooking method and effect of storage temperature on ripening. *Ind. Conserve.*, **55**, 279 (1980)
5. Olafsdottir, G., Steinke, J. A. and Lindsay, R. C. : Quantitative performance of a simple Tenax - GC adsorption method for use in the analysis of aroma volatiles. *J. Food Sci.*, **50**, 1431 (1985)
6. Van den Dool, H. and Kratz, P. D. : A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *J. Chromatog.*, **11**, 463 (1963)
7. Josepson, D. B., Lindsay, R. C. and Stuiber, D. A. : Biogenesis of lipid-derived volatile aroma compounds in the Emerald Shiner (*Notropis atherinoides*). *J. Agric. Food Chem.*, **32**, 1347 (1984)
8. Josepson, D. B., Lindsay, R. C. and Stuiber, D. A. : Variations in the occurrences of enzymatically derived volatile aroma compounds in salt and freshwater fish. *J. Agric. Food Chem.*, **32**, 1344 (1984)
9. Josepson, D. B., Lindsay, R. C. and Stuiber, D. A. : Identification of volatile aroma compounds from oxidized frozen whitefish (*Coregonus clupeaformis*). *Can. Inst. Food Sci. Technol. J.*, **17**, 178 (1984)
10. Josepson, D. B., Lindsay, R. C. and Stuiber, D. A. : Volatile compounds characterizing the aroma of fresh atlantic and pacific oysters. *J. Food Sci.*, **50**, 5 (1985)
11. Josephson, D. B., Lindsay, R. C. and Olafsdottir, G. : *Measurement of volatile aroma constituents as a means for following sensory deterioration of fresh fish and fishery products. Seafood quality determination.* Proceedings of an International Symposium Coordinated by the University of Alaska Sea Grant College Program. Kramer, D. E. and Liston. J.(eds.), p. 27 (1986)
12. Josepson, D. B. and Lindsay, R. C. : Enzymic generation of volatile aroma compounds from fresh fish. Biogeneration of aromas. Symposium series, **317**, p. 201 (1986)
13. Josepson, D. B., Lindsay, R. C. and Stuiber, D. A. : Influence of processing on the volatile compounds characterizing the flavor of pickled fish. *J. Food Sci.*, **52**, 10 (1987)

14 Karahadian, C. and Lindsay, R. C. : Evaluation of compounds contributing characterizing fishy flavors in fish oils. *J. AOCS*, **66**, 953 (1989)
15. Moncrieff, R. W. : In "*The chemical senses*", Wiley : New York, p. 200 (1944)
16. Human, J. and Khayat, A. : Quality evaluation of raw tuna by gas chromatography and sensory methods. *J. Food Sci.*, **46**, 868 (1981)
17. Josepson, D. B., Lindsay, R. C. and Stuiber, D. A. : Identification of compounds characterizing the aroma of fresh whitefish (*Coregonus clupeaformis*). *J. Agric. Food Chem.*, **31**, 326 (1983)
18. Buttery, R. G. : Vegetable and fruit flavors. In "*Flavor research-recent advances*," Terananish R., Flath R. A. and Sugisawa H., (eds.), Marcel Dekker, Inc. New York, NY.p. 175(1981)
19. Withycombe, D. A. and Mussinan, C. J. : Identification of 2-methyl-3-furanthiol in the steam distillate from canned tuna fish. *J. Food'Sci.*, **53**, 658 (1988)

(Received November 15, 1992)

참치 통조림 중 향미 물질의 기원과 품질

김무남† · R.C. Lindsay*

부산여자대학교 식품영양학과†
미국 위스칸신 주립대학교 식품학과*

요 약

참치통조림을 개봉한후 냉장고(4° C)에 4주간 저장하는 동안의 향기변화의 관능검사와 향기성분 분석을 하였다. 막 개봉한 참치통조림의 향은 고소한 쇠고기향과 신선한 참치통조림 특유의 냄새를 가지고 있었으나, card-boardy (1주후), 산화된 지방산 (2주후, 3주후), 그리고 곰팡이냄새와 페인트 냄새 (4주후)로 변하였다. 본 실험에 사용된 참치통조림시료로부터 126개이상의 휘발성성분이 분리되었고, 그중 54개의 화합물이 mass spectral data, IE value, 그리고 GC detector로부터 나오는 efluent를 sniffing하므로서 동정되었다. 4주간 저장 후 저급휘발성 화합물은 줄어드는반면 분자량이 큰화합물이 새로이 생성되었다. 저장지간중 감소된화합물은 1-penten-3-ol, 3-penten-2-ol, heptanal, limonene, 1-pentanol, octanal, 1-hexanol, nonanal, 2-octanone, 2-nonanone, 1-heptanol, benzaldehyde, 그리고 methyl substituted benzene 등이었다. *p*-Thiocresol, 2-chlorophenol, 1,2-dichlorobenzene, dipropyl disulfide, 2-isobutyl-4,5-dimethylthiazole, diethyltrisulfide, 그리고 2-heptylthiophene 은 신선한 참치통조림에는 검출되지않았으나, 개봉후 4주간 저장된 통조림에서는 새로이 검출되었다. 따라서 이들 저장중에 변화된 화합물은 참치 통조림의 품질 변화의 지표로 사용할 수 있을 것으로 생각된다.