EFFECT OF FREEZE STORAGE ON THE VOLATILES OF BUTTER

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SUMMARY: The changes in the volatile components of three butter samples during freeze storage for 7.5 months were studied. The storage led to a significant effect on the separated carbonyl and lactone components. The increase in the yield of the carbonyls caused by peroxidation of unsaturated fatty acids was taken as indication for the deterioration of the butter samples during storage.

Key Words: Butter, fatty acid composition, peroxidation.

INTRODUCTION

Butter is undoubtedly one of the most important foods of man. In addition to its dietary value it has a pleasant aroma.

The identification of a total of 233 compounds in the volatile fractions of butter and butter oil has been reported (1). Stark and his group (2-5) detected the compounds contributed to the flavor of butter oil. They concluded that decanoic acid, lauric acid, δ-octalactone, δ-decalactone, indole and skatole played an important role in the flavor of butter oil.

On the basis of the actual concentration to threshold ratios, butyric and hexanoic acid make no flavor contribution to butter investigated by Urbach *et. al.* (6). On the other hand Mick *et. al.* (7) suggested that, diacetyl, hexanoic acid and δ-decalactone determined the aroma, as their concentrations exceeded their sensory thresholds.

The effect of storage on the butter flavor were studied (8). Badings (9) found a complex mixtures of carbonyl compounds in butter after the cold storage. More recently Widder (10) studied the change in the flavor of butter oil during storage at room temperature for 43 days. They found that among the volatiles formed by lipid peroxidation l-octene-3-one, 2-nonenal and 1,5-octadiene-3-one showed the greatest increase during storage.

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The object of the present work was to detect the effect of freeze-storage for 7.5 months on the volatiles of three different butter samples.

MATERIALS AND METHODS

The samples used were local fresh cow's butter (C), local fresh buffaloe's butter (B) and imported butter purchased from local market (I).

The three butter samples were stored in deep freeze at -18°C for 7.5 months. Samples of each butter were taken at various time periods (1.5, 3, 4.5, 6 and 7.5 months). A sample of each butter before storage (0.0 month) was taken as control.

The volatiles were separated from each butter sample (200 gm) by using the techniques of vacuum steam distillation according to Sike and Lindsay (11). Volatiles were recovered by diethyl ether, dried over anhydrous Na_2SO_4 and concentrated on a Vigreux column (60 x1cm).

Butter fat was separated from each butter sample by melting, decanting and filtering. The fatty acid methyl ester of each sample was prepared (12).

Quantitative analysis of the volatiles and the fatty acid methyl esters of each sample were performed by GLC. The separated components were identified by comparing their retention times with those of authentic samples which were purchased from Aldrich chemical Co.

A Varian 3700 gas chromatography equipped with flame ionization detector and computing integrator was used under the following conditions.

9m x 3mm ID Stainless-steel column, packed with 15% polyethylene glycol adipate (PEGA) on 60-80 mesh chromosorb w; carrier gas (N_2) flow rate 30 ml/min; injector tem-

Table 1: Changes in the volatile components of three butter samples during storage in deep-freeze for 7.5 months.

Peak No	t_R	Local Cow's butter (C)						Local Buffaloe's butter (B)						Imported butter (I)						Components
		0.0	1.5	3.0	4.5	6.0	7.5	0.0	1.5	3.0	4.5	6.0	7.5	0.0	1.5	3.0	4.5	6.0	7.5	
		control	month	month	month	month	month	cont.	mon.	mon.	mon.	mon.	mon.	cont.	mon.	mon.	mon.	mon.	mon.	
1	2.67	7.43*	3.55	3.43	0.93	1.61	0.90	3.33	1.91	1.10	0.91	0.06	5.61	6.27	3.05	1.00	0.50	0.46	0.21	Diacetyl
2	3.14	0.04	0.20	3.86	0.30	5.00	T	T	0.03	0.69	5.08	0.80	1.07	0.09	0.16	0.05	1.18	1.50	2.00	1-Hexene-3-one
3	3.30	0.09	0.11	2.01	6.00	10.32	14.19	T	0.04	0.62	2.25	4.60	5.09	0.53	1.00	0.88	1.09	10.21	14.51	Pentanal
4	3.49	0.27	35.41	34.66	28.79	23.40	6.01	-	3.55	5.07	6.05	10.35	5.06	1.11	2.18	1.98	2.08	26.50	10.99	2-Pentanal
5	4.56	T	0.08	0.12	3.01	18.09	20.25	0.08	2.05	0.10	5.09	15.89	17.04	1.02	0.65	1.77	5.21	40.00	47.41	Hexanal
6	5.43	T	8.00	12.39	6.99	2.15	1.41	0.02	25.17	3.03	6.01	15.01	0.27	2.38	3.09	1.25	1.62	0.71	0.12	2-Hexenal
7	5.48	T	7.40	4.11	4.67	3.60	4.62	-	6.46	0.28	0.51	8.00	0.13	1.11	1.06	0.15	0.20	1.91	0.88	Hexenol
8	5.50	T	T	2.16	2.72	2.68	2.56	0.14	0.03	0.15	2.00	1.11	0.05	2.08	0.19	0.18	0.90	1.09	0.95	Heptanone
9	5.52	T	T	2.87	2.15	2.68	1.09	-	3.11	5.55	0.19	8.55	0.16	0.18	11.05	8.00	9.04	2.09	T	Heptanal
10	5.55	3.52	2.18	7.72	1.55	3.38	4.11	2.00	2.02	9.12	2.14	4.50	0.74	2.06	2.26	1.92	2.23	1.80	1.02	Butyric acid
11	6.68	-	T	0.17	1.50	1.90	2.20	2.22	0.47	0.20	1.02	2.11	1.32	0.20	5.53	10.01	9.80	1.23	1.05	Heptenal
12	7.18	-	-	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	---
13	8.53	-	T	0.16	0.12	T	0.11	0.10	0.05	0.28	0.02	0.02	-	0.11	10.89	0.05	0.08	0.07	0.03	---
14	9.45	-	T	0.79	0.43	0.02	0.08	0.05	0.07	0.51	0.60	0.48	0.32	0.32	0.02	0.04	1.73	0.01	0.10	2-Octenal
15	10.88	3.42	3.91	2.66	1.00	2.05	1.08	T	3.46	1.45	3.46	3.00	8.62	3.04	4.37	2.29	1.00	2.01	1.07	Hexanoic acid
16	11.97	-	0.03	2.05	1.55	0.01	-	2.54	1.04	1.95	1.02	T	0.01	0.13	3.16	2.01	0.08	0.17	0.04	2,4-Heptadienal
17	12.02	0.11	-	0.68	T	0.01	-	-	0.42	1.23	-	-	0.31	0.15	1.09	0.04	0.09	-	-	---
18	12.05	1.66	-	0.40	T	-	-	1.00	0.95	1.81	-	-	0.22	0.45	-	-	T	-	-	---
19	12.13	0.48	0.51	1.01	1.76	2.11	2.99	0.02	0.04	0.37	0.31	0.39	1.16	1.83	0.72	0.64	1.08	1.50	1.04	1-Octene-3-one
20	12.21	0.51	0.50	1.88	5.00	0.49	1.01	0.32	0.12	0.34	-	0.04	0.22	2.48	0.21	0.32	0.23	-	-	---
21	13.97	0.07	0.01	0.01	0.09	T	T	-	0.79	0.27	0.20	0.04	0.16	0.16	0.19	0.24	0.07	0.03	0.17	Nonanal
22	15.35	0.02	0.03	0.37	0.09	0.13	0.16	0.05	0.13	0.35	0.60	0.53	0.24	3.19	0.05	0.16	T	0.21	0.27	2-Nonenal
23	18.15	-	-	0.21	2.60	0.11	0.19	-	1.45	0.85	1.06	0.03	0.74	0.61	0.56	0.81	0.34	0.02	0.18	2,4-Nonadiena
24	20.07	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	---
25	20.53	0.90	-	0.09	0.03	0.20	0.45	0.45	0.26	0.93	0.58	1.15	0.78	37.55	0.48	0.16	0.39	0.17	0.43	---
26	21.42	0.65	0.01	0.45	0.07	0.22	0.67	0.28	0.29	2.18	1.16	0.75	1.28	0.26	0.01	0.21	0.01	0.46	0.42	2,4-Decadienal
27	23.60	-	-	0.11	-	-	0.86	-	0.45	0.49	0.32	0.71	1.28	0.24	1.17	0.04	0.01	0.26	0.27	---
28	24.05	1.17	0.07	0.16	0.01	-	0.67	2.85	0.16	0.63	1.09	0.25	0.28	0.40	0.16	0.06	0.52	0.16	0.06	Undecanone
29	25.37	0.31	-	0.02	1.02	0.67	-	1.22	1.35	9.26	0.78	0.03	0.58	2.38	0.34	0.39	0.16	0.28	0.17	---
30	26.36	0.03	0.05	0.16	5.47	0.95	0.90	0.26	0.23	12.84	1.52	0.22	0.51	0.17	0.22	0.07	0.16	0.60	0.27	Undecadienal
31	28.20	0.44	0.03	0.13	-	-	0.09	0.40	0.18	1.67	0.04	0.59	0.38	0.15	0.26	-	0.33	0.16	0.03	---
32	29.96	1.03	0.03	0.22	0.11	0.89	0.24	0.35	0.17	0.64	1.98	-	0.22	1.41	0.06	0.03	0.47	0.12	0.01	Dodecanone
33	31.15	6.14	0.08	0.39	0.50	1.62	0.24	14.60	0.53	0.83	0.94	0.49	0.20	1.52	0.44	0.17	38.18	0.07	0.09	δ-Octalactone
34	33.60	1.09	0.07	0.27	0.30	1.23	0.14	4.00	0.28	2.95	6.19	0.23	0.02	3.27	0.52	43.04	1.59	0.61	0.06	Octanic acid
35	35.46	2.00	-	0.09	-	0.04	0.16	-	5.29	5.26	4.01	-	0.01	-	0.13	0.26	1.52	0.01	0.02	---
36	36.30	14.22	2.00	0.03	0.30	0.10	0.86	1.48	0.84	2.25	8.29	0.18	0.65	3.97	1.17	0.20	1.91	0.13	0.49	δ-Decalactone
37	38.20	2.40	3.64	0.46	0.10	0.32	T	2.00	0.86	0.25	6.75	0.92	0.03	1.84	0.28	1.85	0.18	0.06	0.08	---
38	40.81	0.79	T	0.10	3.26	2.59	1.89	1.00	0.33	0.25	1.42	0.03	0.71	T	0.90	0.63	2.38	0.09	T	Dodecadienal
39	41.50	38.30	8.26	1.29	5.17	4.17	24.44	30.30	2.00	7.78	5.38	9.27	2.99	10.20	1.77	3.24	1.91	1.83	11.69	δ-Dodecalacton
40	44.30	0.11	-	0.64	0.17	1.65	3.11	10.06	1.87	0.02	0.52	1.97	28.21	2.33	0.10	3.44	1.69	0.12	0.46	g-Dodecalactone
41	46.60	1.11	3.39	0.52	4.55	3.48	1.07	2.07	2.85	2.16	3.40	3.82	2.09	1.43	3.43	2.60	2.73	0.23	0.84	Deconic acid-
42	47.17	0.31	3.00	4.16	1.47	0.14	-	0.70	2.32	2.21	1.40	0.28	2.19	-	0.96	2.37	1.99	0.26	0.53	---
43	48.50	-	-	0.20	1.22	0.48	0.24	1.71	6.25	3.18	2.62	1.57	0.17	-	3.55	-	2.96	0.65	T	---
44	49.60	3.55	5.49	0.26	0.39	0.39	0.58	7.39	3.51	3.65	2.51	0.53	0.80	0.90	1.69	1.62	1.38	0.53	0.42	δ-Tetradecalactone
45	50.70	0.64	1.90	0.32	0.23	0.24	0.05	2.53	1.88	2.85	1.76	0.46	2.14	0.48	1.13	1.88	0.04	0.46	0.36	Ethyl tetradecanoic acid
46	51.90	0.11	2.00	0.32	0.19	0.73	0.38	-	5.29	1.05	2.59	0.19	1.60	-	0.51	1.76	0.08	0.15	0.61	
47	53.40	3.52	3.37	0.81	1.01	0.75	-	0.06	6.37	6.30	0.22	0.71	1.23	-	0.02	0.95	0.75	0.43	0.45	
48	56.60	0.78	1.14	T	0.02	T	-	0.32	2.24	2.00	6.01	0.14	3.99	-	0.11	1.24	0.11	0.42	0.13	
49	57.70	2.88	3.12	5.08	T	T	T	0.10	0.84	1.05	-	-	0.50	-	0.07	-	0.04	0.21	0.07	
50	59.00	-	0.44	T	0.15	-	-	-	-	-	-	-	-	-	0.04	-	-	0.01	-	

Table 2: The change in the fatty acid composition of the freeze stored butter fat.

Fatty acids	Local Buffaloe's butter (B)						Local Cow's butter (C)						Imported butter (I)					
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
C_4	4.81	4.70	4.19	3.71	2.23	2.30	4.14	4.35	3.69	2.02	2.66	3.50	3.43	3.43	3.24	3.68	3.02	3.43
C_6	3.60	3.52	2.46	3.26	1.17	1.50	2.66	3.02	2.31	1.72	2.14	2.10	2.72	2.78	2.84	3.04	2.44	2.41
C_8	1.40	1.71	1.30	1.50	1.65	1.55	1.44	2.90	2.38	0.95	1.27	1.00	1.63	1.91	1.86	1.73	1.78	1.86
C_{10}	3.15	3.33	2.66	3.11	1.57	1.63	3.27	3.24	3.11	1.30	2.97	1.50	3.85	3.95	4.42	4.34	4.69	4.63
C_{12}	3.21	2.60	2.45	4.02	2.08	2.03	3.75	3.56	1.09	4.29	3.64	3.15	4.31	4.61	4.89	4.22	4.58	4.28
C_{14}	11.71	12.75	12.55	12.90	15.97	14.06	11.64	11.40	12.33	9.68	11.14	11.51	11.78	11.65	12.25	12.00	12.93	13.01
$C_{14:1}$	1.78	1.71	2.38	2.28	1.84	1.71	2.17	2.51	1.96	2.89	1.64	1.85	1.86	1.81	2.23	2.37	1.29	1.25
$C_{14:2}$	2.02	2.11	1.97	2.75	0.99	0.81	2.76	2.61	3.59	3.65	2.35	2.13	2.15	2.07	3.33	2.63	2.34	1.77
$C_{16\ iso}$	3.09	2.91	2.94	2.43	1.34	1.53	3.71	3.92	3.42	3.29	3.25	3.25	2.62	3.16	4.16	3.36	2.18	1.51
C_{16}	25.59	26.54	26.95	27.21	32.98	34.82	26.72	27.19	39.76	30.23	30.56	30.63	26.01	26.05	27.71	27.43	29.02	30.81
$C_{16:1}$	0.50	0.50	2.66	2.02	2.42	2.11	0.64	2.35	2.79	3.11	2.12	2.31	2.05	2.11	2.85	1.21	2.16	2.52
$C_{16:2}$	2.17	0.78	1.69	1.36	1.34	1.33	2.76	1.87	2.95	3.44	1.16	1.80	3.03	2.87	2.82	1.49	1.09	0.91
C_{17}	1.38	1.11	-	-	-	-	1.72	-	-	2.5	-	-	1.95	1.85	-	T	-	-
C_{18}	13.61	13.91	13.91	12.69	13.45	14.0	10.65	10.80	11.34	10.77	11.73	11.96	11.12	11.33	11.58	12.28	12.24	12.11
$C_{18:1}$	20.40	20.51	21.16	20.14	20.79	20.62	19.94	19.17	21.19	19.04	23.22	22.80	19.02	19.31	20.84	20.22	20.24	19.50
$C_{18:2}$	1.11	1.01	0.50	0.44	0.18	-	1.36	0.60	0.59	0.45	0.05	-	1.32	1.10	0.45	-	-	-
$C_{18:3}$	0.47	0.30	0.23	0.18	-	-	0.67	0.51	0.45	0.37	T	T	1.15	0.51	0.33	-	-	-
C_{19}	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_{20}	T	T	-	-	-	-	T	T	-	-	-	-	-	T	-	-	-	-

perature, 220°C; detector temperature 250°C, oven temperature, (programming) 70-190°C (4°C/min).

RESULTS AND DISCUSSION

The principal volatile components of the three investigated samples, cow's butter (C), buffaloe's butter (B) and imported butter (I) stored in the deep freeze for 0.0 (control), 1.5, 3, 4.5, 6 and 7.5 months are reported in Table 1.

The carbonyl components comprised the major qualitatively contribution in the Table. Diacetyl had considerable concentration in the three butter samples, this component plays an important role in the aroma of butter (13). 2-Hexenal, 2-pentenal and 2,4-heptadienal increased during storage in the three investigated samples, however their concentration decreased at the end of storage (7.5 months). The formation of these components consistent with the peroxidation of Linolenate (14,15). These results agreed with the observed decrease in linolenic acid (Table 2).

Heptanal, 2-octenal, 2-nonenal, 2,4-nonadienal and 2,4-decadienal showed the same trend, whereas pentanal and hexanal had their highest concentrations by storage for 7.5 months. All these aldehydes are peroxidation products of linolenic acid (16) which showed gradual decrease during storage (Table 2). Pentanal was reported to arise from stepwise oxidation of nonanal through C_8-C_4 Alkanals (17).

The second important class of volatiles consist of lactones. Table 1 shows that five lactones were isolated among them δ-dodecalactone was the predominant component in the control of samples C and B (38.30% and 30.30%, respectively) whereas it was identified with less concentration (10.20%) in control of sample I.

δ-Octalactone showed high concentration (14.60%) in control of sample B while d-decalactone had nearly equal concentration (14.22%) in sample C. The usual description of lactones flavor has been coconut (6).

Four free fatty acids were identified in the investigated butter samples (Table 1). δ-Lactones and free fatty acids have been considered as important flavor components in dairy product (4).

However, on the basis of the actual concentration to threshold ratios. Urbach (6) and Stark *et. al.* (4) reported that butyric and hexanoic acids make no flavor contribution to butter.

Table 3: Changes in the total concentration of volatile carbonyls and lactones of butter samples during freeze storage (values expressed as area percentages).

Chemical classes	Local Buffaloe's butter (B)						Local Cow's butter (C)						Imported butter (I)					
	0.0	1.5	3.0	4.5	6.0	7.5	0.0	1.5	3.0	4.5	6.0	7.5	0.0	1.5	3.0	4.5	6.0	7.5
	control	month	month	month	month	month	cont.	mon.	mon.	mon.	mon.	mon.	cont.	mon.	mon.	mon.	mon.	mon.
Carbonyls	16.09	41.06	37.35	39.56	55.2	43.73	12.07	48.08	67.2	67.83	74.86	56.41	22.34	32.95	32.77	38.26	87.16	79.8
Lactones	48.10	7.01	14.53	31.56	12.44	32.49	58.11	15.83	1.61	6.53	7.93	30.23	18.92	4.58	52.81	46.89	2.68	13.15

In view of the results reported in Table 1, it is clear that freeze storage of the three butter samples led to a significant effect on the separated carbonyls and lactones. In order to elucidate this effect, the total area percentages of these two chemical classes were determined and cited in Table 3. The data in the table show that, the freeze storage gave rise to a gradual increase in the total yield of the carbonyls reaching their maximum value after 4.5 months followed by a noticeable decrease at the end of storage, this decrease may be attributed to the loss of some volatile carbonyl components during storage. These results coincide with those obtained by Badings (9).

From the data shown in Table 3, it is clear that, there is no regular behavior for the yield of lactone components during storage. Samples C and B had the maximum value in their control samples, whereas sample I showed the highest yield after storage for 3.0 months. δ-Lactones are the conversion products of δ-hydroxy acids present in butter (18).

From the above mentioned results, it is clear that, the yield of the carbonyls which caused by peroxidation of fatty acids can be used as indication for the deterioration of the butter samples during storage.

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