



IMPROVING KEEPING QUALITY OF BUTTER BY UTILIZING MAILLARD REACTION PRODUCTS FROM HEATED WHEY

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Keywords: Antioxidant, Maillard reaction products (MRPs), Peroxide value, Thiobarbituric acid, Butter fat oxidation

ABSTRACT

The antioxidative activity of Maillard reaction products (MRPs) from heated whey added to butter was investigated. The antioxidant efficiency changed with different concentrations of MRPs used during storage period at 45°C. Peroxide value, thiobarbituric acid, acid value, carbonyl compounds and free fatty acids of butter were increased with storage. Their rate of increase decreased with increasing the added amount of MRPs to butter.

INTRODUCTION

The major deteriorative reaction in butter is fat oxidation which leads to the development of objectionable flavour and odours consequently loss in the quality of butter. The Maillard reaction products have been shown to possess antioxidative properties Hassan *et al* (2005) and Namiki, (1988). Investigations have shown that there is an interaction of sugars with amino acid Hawang and Kim (1973), peptides protein hydrolysates Lingnert and Eriksson (1980) and milk proteins Taylor and Richardson (1980). The resistance of heated whey to oxidation was believed to be due to the liberation of sulphhydryl groups McGookin and Augustin (1991), but it has been shown that sulphhydryls play only a minor role in its antioxidant activity of heated whey Taylor and Richardson (1980).

Autooxidation and lipo lysis of lipids are responsible for off-flavours in lipid-containing food products. Butter deteriorates by reaction with atmospheric oxygen and hydrolytic reactions cata-

lyzed by lipases from food or from microorganisms Farag, *et al* (1989) and Allen and Wrienden (1982).

Synthetic antioxidants such as propylgallate, butylated hydroxy anisole and butylated hydroxy toluene are added to food products in order to retard lipid oxidation Allen and Wrienden (1982).

However, these synthetic substances may have harmful effects at certain levels on humans, since butylated hydroxy anisole had toxic and carcinogenic effect Alaiz, *et al* (1997). Also, butylated hydroxy toluene causes changes in rat thyroids, stimulation for DNA synthesis and induction of enzymes Hassan, *et al* (2005) and Lingnert and Eriksson (1981).

The trend in recent years has been centered on the use of natural compounds as food preservative. Therefore, there is an urgent need for other types of antioxidant compounds causing no harmful effect on humans.

The aim of this study was to assess the antioxidant activity of Maillard reaction products obtained from heated sweet whey when added to butter.

MATERIALS AND METHODS

I- Materials

Buffaloe's butter and fresh sweet whey were obtained from the department of Dairy Technology, Animal Production Research Institute, Agriculture Research Center Dokki, Egypt.

Preparation of Maillard Reaction Products (MRPs)

Sweet fresh whey was heated to 121°C for 1hr. in an autoclave. After heating the obtained solution was filtered and cooled immediately to <25°C. This coloured solution was tested for browning intensity which represent MRPs.

Incorporation of MRPs into butter

Butter was divided into six portions, the first one was served as control. 0.2%, 0.4%, 0.6%, 0.8% and 1.0% of treated whey were thoroughly mixed with the other five portions, respectively. Samples were stored under accelerating deteriorative temperature being 45°C and analyzed when fresh and weekly for twelve weeks for fat deterioration tests.

II- Methods

Determination of browning

The method described by **Moralas and Van Boekel (1998)** was applied to determine the colour intensity. In this method one ml of sample was taken and absorbance, after dilution 1:2 in water was measured at 420 and 550nm. Absorbance at 420 nm was corrected for any turbidity by subtracting the absorbance at 550nm. The blank value obtained from an unheated sample was subtracted from the sample reading.

Peroxide value

The method described by **IDF (1974)** was used. In this method a known weight of butter was dissolved in a mixture of methanol, chloroform (30:70 v/v). Then 0.05 ml of ammonium thiocyanate solution (30%w/v) and mixed thoroughly. Thereafter, 0.05ml of iron chloride solution was added. After 5 min. the obtained solution was measured at 500 nm.

Thiobarbituric acid test (TBA)

TBA value was determined according to the method described by **Keeney (1971)**. Reagent (6ml, 0.025N) and trichloroacetic acid (3ml, 20%). A known weight of butter was thoroughly mixed with TBA and heated in a boiling water bath for 20 min. The interfering substances were extracted three times with ether (20ml each) and discarded. The aqueous phase was completed with distilled water to a known volume and the absorbance of this solution was recorded at 532 nm.

Acid value and free fatty acid (FFA)

Acid value and free fatty acids content (as oleic acid) were determined in butter samples as the described method mentioned in **IDF (1969)**.

Total carbonyl compounds

Total carbonyl compound content of butter samples was determined by the method described by **Berry and McKerrigan (1958)**.

Statistical analysis

The obtained data were statistically analyzed according to **SAS (1996)**.

RESULTS AND DISCUSSION

Maillard reaction was carried out by heating sweet fresh whey as mentioned previously under Materials and Methods. Colour intensity was used as indicator to MRPs.

1- Peroxide value

Data presented in **Table (1)** show the effect of adding Maillard reaction products resulted from heat treated whey to butter on peroxide value. It is clear from the data that the peroxide value of all treatments increased significantly with storage period. **McGookin and Augustin (1991)** mentioned that, the peroxide values increased with time.

Also, the data show that, the rate of increasing peroxide value of control butter was the highest compared to the other treatments. The rate of developing peroxide value during storage period at 45°C was affected significantly with the concentration of MRPs added to butter which decreased with increasing the added level.

2- Thiobarbituric acid (TBA)

Thiobarbituric acid is the second parameter used to follow up the antioxidative effect of MRPs.

Data presented in **Table (2)** summarize the TBA values development in butter samples treated with different MRPs levels.

Table 1. Effect of Maillard reaction products (MRPs) from whey on butter peroxide value (m. equiv. O₂/kg fat) during storage at 45°C

Storage period (weeks)	Control	Added MRPs				
		0.2%	0.40%	0.6%	0.8%	1.0%
Fresh	0.38 ^{Aa}	0.37 ^{Aa}	0.38 ^{Aa}	0.38 ^{Aa}	0.36 ^{Aa}	0.38 ^{Aa}
1	0.42 ^{Aa}	0.41 ^{Aa}	0.40 ^{Aa}	0.39 ^{Aa}	0.38 ^{Aa}	0.38 ^{Aa}
2	0.63 ^{Ad}	0.58 ^{Ad}	0.54 ^{Ac}	0.51 ^{Ab}	0.48 ^{Ab}	0.41 ^{Aa}
3	0.88 ^{Ad}	0.73 ^{Ac}	0.69 ^{Bb}	0.63 ^{Ab}	0.59 ^{Ba}	0.52 ^{Ba}
4	0.96 ^{Ad}	0.81 ^{Bc}	0.73 ^{Bb}	0.68 ^{Ba}	0.64 ^{Ba}	0.57 ^{Ba}
5	1.17 ^{Ad}	0.89 ^{Bb}	0.76 ^{Bb}	0.71 ^{Ba}	0.68 ^{Ba}	0.60 ^{Ba}
6	1.43 ^{Bd}	0.93 ^{Bb}	0.79 ^{Ba}	0.75 ^{Ba}	0.70 ^{Ba}	0.62 ^{Ba}
7	1.79 ^{Bc}	1.01 ^{Bb}	0.85 ^{Ba}	0.78 ^{Ca}	0.73 ^{Ca}	0.64 ^{Ca}
8	2.01 ^{Bd}	1.13 ^{Ba}	0.92 ^{Ca}	0.85 ^{Ca}	0.77 ^{Ca}	0.68 ^{Ca}
9	2.79 ^{Cd}	1.27 ^{Ca}	1.03 ^{Ca}	0.91 ^{Ca}	0.83 ^{Ca}	0.71 ^{Ca}
10	3.05 ^{Cd}	1.46 ^{Ca}	1.11 ^{Ca}	0.99 ^{Da}	0.89 ^{Ca}	0.78 ^{Da}
11	3.62 ^{Dd}	1.65 ^{Da}	1.23 ^{Da}	1.07 ^{Da}	0.96 ^{Da}	0.82 ^{Da}
12	4.13 ^{Dd}	1.91 ^{Da}	1.38 ^{Da}	1.13 ^{Da}	1.09 ^{Da}	0.89 ^{Da}

Means with different letters are significantly different (P<0.05).

Table 2. Effect of Maillard reaction products (MRPs) from whey on TBA value of butter during storage at 45°C

Storage period (weeks)	Control	Added MRPs				
		0.2%	0.40%	0.6%	0.8%	1.0%
Fresh	0.008 ^{Aa}	0.006 ^{Aa}	0.004 ^{Aa}	0.003 ^{Aa}	0.001 ^{Aa}	0.000 ^{Aa}
1	0.012 ^{Ad}	0.009 ^{Aa}	0.007 ^{Aa}	0.005 ^{Aa}	0.004 ^{Aa}	0.002 ^{Aa}
2	0.016 ^{Ad}	0.011 ^{Aa}	0.010 ^{Aa}	0.008 ^{Aa}	0.006 ^{Aa}	0.005 ^{Aa}
3	0.019 ^{Bd}	0.016 ^{Bc}	0.013 ^{Bb}	0.010 ^{Aa}	0.009 ^{Aa}	0.007 ^{Aa}
4	0.022 ^{Bd}	0.018 ^{Bc}	0.016 ^{Bc}	0.014 ^{Bb}	0.012 ^{Ab}	0.008 ^{Aa}
5	0.026 ^{Bd}	0.021 ^{Bc}	0.019 ^{Bc}	0.015 ^{Bb}	0.013 ^{Ba}	0.009 ^{Aa}
6	0.028 ^{Cd}	0.024 ^{Bc}	0.022 ^{Bc}	0.016 ^{Bd}	0.014 ^{Ba}	0.010 ^{Aa}
7	0.033 ^{Cd}	0.026 ^{Cc}	0.024 ^{Bc}	0.018 ^{Bd}	0.016 ^{Ba}	0.012 ^{Aa}
8	0.038 ^{Dd}	0.028 ^{Cc}	0.026 ^{Cb}	0.024 ^{Bb}	0.018 ^{Ba}	0.014 ^{Ba}
9	0.041 ^{Dd}	0.029 ^{Cc}	0.027 ^{Cb}	0.025 ^{Cb}	0.020 ^{Ba}	0.015 ^{Ba}
10	0.046 ^{Dd}	0.030 ^{Cb}	0.028 ^{Cb}	0.026 ^{Cb}	0.022 ^{Ba}	0.016 ^{Ba}
11	0.047 ^{Dd}	0.031 ^{Cb}	0.030 ^{Cb}	0.027 ^{Cb}	0.024 ^{Ba}	0.017 ^{Ba}
12	0.048 ^{Dd}	0.033 ^{Cb}	0.031 ^{Cb}	0.028 ^{Cb}	0.026 ^{Ca}	0.018 ^{Ba}

Means with different letters are significantly different (P<0.05).

It is clear that TBA values increased significantly and gradually during storage and these values were lower in treatments than in control. Also, the data show that the rate of increasing in TBA values decreased significantly with increasing the concentration of added MRPs. Farag *et al* (1989) mentioned that the inhibitory effect of antioxidants has been attributed to their donation of electrons of hydrogen atoms from the phenolic hydroxyl groups to oil containing free radical which do not initiate nor propagate further oxidation of oils.

3- Acid value

Data presented in Table (3) show the acid value of butter during storage at 45°C and the effect of adding MRPs.

It obvious from the data that butter acid value increased significantly in all treatments with storage. Also, the data show that acid value affected significantly with the concentration of MRPs used. The rate of increasing the acid value reduced with increasing the concentration of MRPs. Abd El-Gawad (1992) found an increase in acid value with storage of butter oil even at 40°C.

4- Free fatty acids (FFA)

Butter free fatty acids content when fresh and during storage at 40°C as affected by addition of MRPs from heated sweet whey are shown in Table (4). The FFA of all treatments increased significantly with storage and the rate of increasing decreased significantly with increasing the added MRPs level. These results are in agreement with Abd El-Gawad (1992) who mentioned that free fatty acids of butter and butter oil increased when stored at 40°C.

5- Total carbonyl compounds (TCC)

Effect of adding MRPs to butter on its total carbonyl compounds content when fresh or during storage at 45°C are shown in Table (5).

It is clear from the data that TCC of butter increased significantly with storage for control and all treatments. These results are in agreement with the finding of Labuschagne (1972) and Labuschagne, *et al* (1973) who found an increase in TCC in butter due to storage either at 20 or 10°C.

Also, butter TCC content affected significantly with the added amount of MRPs. The TCC values decreased with increasing MRPs addition.

Table 3. Effect of Maillard reaction products (MRPs) from whey on butter acid value (mg KOH/1g fat) during storage at 45°C

Storage period (weeks)	Control	Added MRPs				
		0.2%	0.40%	0.6%	0.8%	1.0%
Fresh	0.64 ^{Aa}	0.63 ^{Aa}	0.63 ^{Aa}	0.64 ^{Aa}	0.64 ^{Aa}	0.63 ^{Aa}
1	1.43 ^{Ad}	1.32 ^{Ac}	1.25 ^{Ac}	1.18 ^{Ab}	1.10 ^{Aa}	1.01 ^{Aa}
2	3.20 ^{Bd}	2.46 ^{Bb}	1.49 ^{Aa}	1.32 ^{Aa}	1.28 ^{Aa}	1.24 ^{Aa}
3	4.76 ^{Cd}	2.98 ^{Bb}	1.87 ^{Aa}	1.65 ^{Aa}	1.49 ^{Aa}	1.38 ^{Aa}
4	5.86 ^{Cd}	3.56 ^{Bb}	2.27 ^{Aa}	2.01 ^{Aa}	1.82 ^{Aa}	1.72 ^{Aa}
5	6.06 ^{Cd}	3.85 ^{Bb}	2.92 ^{Ba}	2.74 ^{Ba}	2.13 ^{Aa}	1.95 ^{Aa}
6	6.72 ^{Dd}	4.28 ^{Bb}	3.18 ^{Ba}	2.80 ^{Ba}	2.70 ^{Aa}	2.62 ^{Ba}
7	7.11 ^{Dd}	4.39 ^{Ca}	3.91 ^{Ba}	3.75 ^{Ba}	3.61 ^{Aa}	3.57 ^{Ba}
8	7.34 ^{Dd}	4.64 ^{Ca}	4.42 ^{Ba}	4.36 ^{Ca}	4.28 ^{Ba}	4.20 ^{Ba}
9	7.48 ^{Dd}	4.68 ^{Ca}	4.52 ^{Ca}	4.47 ^{Ca}	4.31 ^{Ca}	4.25 ^{Ba}
10	7.63 ^{Dd}	4.71 ^{Ca}	4.60 ^{Ca}	4.49 ^{Ca}	4.38 ^C	4.27 ^{Ba}
11	7.76 ^{Dd}	4.82 ^{Ca}	4.69 ^{Ca}	4.58 ^{Ca}	4.44 ^C	4.31 ^{Ca}
12	7.85 ^{Dd}	4.94 ^{Ca}	4.83 ^{Ca}	4.71 ^{Ca}	4.49 ^C	4.38 ^{Ca}

Means with different letters are significantly different (P<0.05).

Table 4. Effect of Maillard reaction products (MRPs) from whey on free fatty acids percentage (as oleic acid) of butter during storage at 45°C

Storage period (weeks)	Control	Added MRPs				
		0.2%	0.40%	0.6%	0.8%	1.0%
Fresh	0.282 ^{Aa}	0.282 ^{Aa}	0.285 ^{Aa}	0.284 ^{Aa}	0.281 ^{Aa}	0.282 ^{Aa}
1	0.658 ^{Ad}	0.543 ^{Ac}	0.442 ^{Ab}	0.417 ^{Ab}	0.396 ^{Aa}	0.387 ^{Aa}
2	1.610 ^{Bd}	1.240 ^{Ac}	0.943 ^{Ab}	0.663 ^{Aa}	0.643 ^{Aa}	0.626 ^{Aa}
3	2.001 ^{Bd}	1.582 ^{Bd}	1.093 ^{Aa}	0.879 ^{Aa}	0.811 ^{Aa}	0.721 ^{Aa}
4	2.950 ^{Cd}	1.790 ^{Bc}	1.141 ^{Ab}	1.010 ^{Aa}	0.919 ^{Aa}	0.865 ^{Aa}
5	3.11 ^{Dd}	1.925 ^{Bc}	1.279 ^{Bb}	1.109 ^{Aa}	1.007 ^{Aa}	0.952 ^{Aa}
6	3.38 ^{Dd}	2.152 ^{Cc}	1.600 ^{Bb}	1.410 ^{Aa}	1.360 ^{Ba}	1.320 ^{Ba}
7	3.511 ^{Dd}	2.203 ^{Cc}	1.988 ^{Bb}	1.792 ^{Ba}	1.654 ^{Ba}	1.555 ^{Ba}
8	3.670 ^{Dd}	2.335 ^{Cb}	2.202 ^{Ca}	2.140 ^{Ba}	2.135 ^{Ba}	2.110 ^{Ba}
9	3.726 ^{Dd}	2.710 ^{Cb}	2.288 ^{Ca}	2.197 ^{Ca}	2.182 ^{Ca}	2.121 ^{Ba}
10	3.840 ^{Dd}	2.870 ^{Cb}	2.310 ^{Ca}	2.260 ^{Ca}	2.210 ^{Ca}	2.140 ^{Ca}
11	3.907 ^{Dd}	3.002 ^{Cb}	2.391 ^{Ca}	2.301 ^{Ca}	2.252 ^{Ca}	2.196 ^{Ca}
12	3.950 ^{Dd}	3.480 ^{Db}	2.430 ^{Ca}	2.370 ^{Ca}	2.280 ^{Ca}	2.200 ^{Ca}

Means with different letters are significantly different ($P < 0.05$)

Table 5. Effect of Maillard reaction products (MRPs) from whey on total carbonyl compounds content of butter ($\mu\text{mol}/\text{kg}$ fat) during storage at 45°C

Storage period (weeks)	Control	Added MRPs				
		0.2%	0.40%	0.6%	0.8%	1.0%
Fresh	1.85 ^{Aa}	1.87 ^{Aa}	1.83 ^{Aa}	1.84 ^{Aa}	1.87 ^{Aa}	1.86 ^{Aa}
1	2.22 ^{Aa}	2.49 ^{Aa}	2.35 ^{Aa}	2.47 ^{Aa}	2.31 ^{Aa}	1.97 ^{Aa}
2	2.87 ^{Ad}	2.65 ^{Ac}	2.50 ^{Ac}	2.44 ^{Ab}	2.36 ^{Ab}	2.08 ^{Aa}
3	3.25 ^{Ad}	2.99 ^{Ac}	2.87 ^{Ac}	2.74 ^{Ac}	2.58 ^{Ab}	2.11 ^{Aa}
4	4.53 ^{Ab}	3.34 ^{Ab}	3.22 ^{Ab}	3.18 ^{Ab}	2.84 ^{Aa}	2.28 ^{Aa}
5	4.96 ^{Ad}	4.11 ^{Ac}	4.01 ^{Ac}	3.32 ^{Ab}	3.15 ^{Ab}	2.33 ^{Aa}
6	5.48 ^{Bd}	4.54 ^{Ac}	4.46 ^{Ac}	3.52 ^{Ab}	3.38 ^{Ab}	2.41 ^{Ac}
7	7.15 ^{Bd}	4.82 ^{Ab}	4.59 ^{Ab}	3.87 ^{Ab}	3.54 ^{Aa}	2.55 ^{Aa}
8	8.14 ^{Cd}	5.20 ^{Ba}	4.66 ^{Aa}	4.00 ^{Aa}	3.58 ^{Aa}	2.60 ^{Aa}
9	9.18 ^{Cd}	5.79 ^{Bb}	4.98 ^{Ab}	4.25 ^{Aa}	3.61 ^{Aa}	2.78 ^{Aa}
10	11.28 ^{Dd}	6.18 ^{Bb}	5.26 ^{Bb}	4.32 ^{Aa}	3.68 ^{Aa}	2.91 ^{Aa}
11	12.50 ^{Dd}	6.41 ^{Bb}	5.93 ^{Bb}	4.62 ^{Aa}	3.91 ^{Aa}	3.05 ^{Aa}
12	14.08 ^{Dd}	6.59 ^{Bb}	6.14 ^{Bb}	4.82 ^{Aa}	4.11 ^{Aa}	3.19 ^{Aa}

Means with different letters are significantly different ($P < 0.05$).

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مجلد (١٥)، عدد (١)، ١١٣-١١٩، ٢٠٠٧

تحسين قوة حفظ الزيت بالاستفادة من نواتج تفاعل ميلارد من الشرش المسخن

[١٠]

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ميلارد من الشرش غير لملح وذلك بتسخينه لدرجة حرارة ١٢١م^٥/ساعة وتنت إضافة إلى الزيت بنسب ٠,٢% ، ٠,٤% ، ٠,٦% ، ٠,٨% ، ١% بالإضافة إلى معاملة المقارنة بدون إضافة. وتم تتبع الفعل المضاد للأكسدة أثناء تخزين معاملات الزيت المختلفة تحت ظروف حرارة مرتفعة ٤٥م^٥ لإسراع إحداث التغيرات أثناء التخزين ولادة ١٢ أسبوع. ولقد تزايدت قيم كل من رقم البيروكسيد وحمض الثيوباربيتوريك ورقم الحمض ومركبات الكربونيل بالإضافة إلى الأحماض الدهنية الحرة أثناء التخزين وأن معدل الزيادة انخفض بزيادة كمية نواتج تفاعل ميلارد المضافة للزبد مازنة بالعينة المقارنة التي بدون إضافات.

أكسدة وتحلل الدهن من المشاكل الكبيرة التي تسبب ضعف قوة حفظ الأغذية المحتوية على زيوت أو دهون وتؤخر من حدوث ذلك تواجد مركبات مضادة للأكسدة سواء كانت طبيعية أو تركيبية. وغالبا ما يلجأ القائمين بالتصنيع إلى إضافة مثل هذه المواد لزيادة قوة الحفظ وحيث أن المواد المضافة التركيبية غالبا ما تكون ذات تأثيرات صحية سلبية. وتتركز الجهود العالمية حاليا نحو استعمال مضادات أكسدة أو مادة حافظة في الأغذية من مصادر طبيعية لا تسبب أضرار صحية للإنسان ذلك كان هدف البحث الحالي هو تقييم النشاط المضاد للأكسدة لنواتج تفاعل ميلارد في الشرش المسخن عند إضافتها إلى الزيت بهدف تحسين قوة الحفظ. تم الحصول على نواتج تفاعل