THE EFFECT OF THE BROWNING REACTION ON STABILITY OF STORED SUGAR COOKIES

by

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TABLE OF CONTENTS

INTRODUCTION

The economic importance of the browning reaction was recognized during World War II. Prior to this period the reaction was little more than a laboratory curiosity. The increased demand by our armed forces for dried and other types of stable foods initiated intensive research programs. It was recognized that the browning reaction imparted detrimental characteristics to some foods. This occurred primarily in foods such as dried milk, eggs, and fruits which contain a high percentage of protein and reducing sugars. However, the browning reaction is not always a detrimental factor. In many foods it is recognized as causing desirable odors and color.

There are several types of browning reactions in food products. These may be classified in three broad groups; (1) caramelization, (2) oxidative browning, and (3) the carbonyl-amine reaction. Carmelization occurs when polyhydroxy carbonyl compounds, such as sugars, are heated to high temperatures in the absence of amino acids. This reaction requires a great amount of energy to occur. Oxidative browning is usually enzymatic and is primarily of importance in the fruit industry. This browning occurs by the oxidative polymerization or condensation of carbonyl and polycarbonyl compounds. The third type occurs as a result of the reaction between carbonyl and amino acompounds and is commonly referred to as the Maillard reaction. An illustration of this is the condensation of reducing sugars with the amino groups of proteins.

The major cause of browning in bakery products is the Maillard or carbonyl-amino type of browning (18). The recent literature concerning Maillard type browning is voluminous (29). However, most of the literature treating the browning reaction concerns model systems and foods other than bakery products.

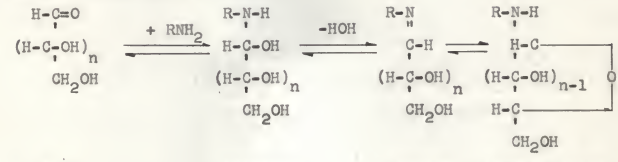
The Primary Carbonyl-Amino Reaction

The mechanism of the Maillard type reaction is very complex. Maillard (38) postulated that the active group of the sugars react with an amino group to form a Schiff base. Decarboxylation and dehydration of this product yields the dark melanoidin pigments. It was thought that the carbon dioxide liberated originated from the carboxyl group of the amino acid. This has recently been confirmed by use of radio active tracer techniques (46, 50).

The initial condensation of an amino acid and a reducing sugar in a 1 to 1 ratio have been observed by several workers (19, 20, 36, 39). Hannan and Lea (19) isolated a 1 to 1 reaction product from a freeze-dried glucose -α- N-acetyl-l-lysine reaction mixture by paper chromatography. Stadtman et al. (46), using C^{14} labeled glucose and glycine with unlabeled glucose and glycine, showed that the major reaction product was derived from glucose and glycine. This compound was separated by chromatographic techniques and elemental analysis indicated that it was a 1 to 1 condensation product.

The accepted mechanism of sugar-amine condensation involves opening of the ring form of the sugar (I), addition of the amine

(II), and the elimination of one mole of water to form the Schiff base (III) which is in equilibrium with the ^{N}-substituted glycosylamine (IV) (28).



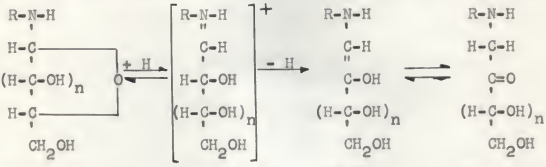
Aldose (aldehyde form) I | Addition compound II | Schiff base III | N-substituted glycosylamine IV

Diglycosylamines also may be formed in sugar-amine reactions (5). Mohammad et al. (39) and Lea and Hannan (19, 32, 33) showed that the sugar-amine reaction initially is a 1 to 1 reaction product but in the latter stages the ratio may approach 1.5 to 1 (glucose to glycine).

The formation of the N-substituted glycoside was not altogether tenable as the browning reaction systems exhibited many properties that cannot be accounted for by this compound. After the sugar-amine reaction the glucose portion cannot be liberated by acid or base hydrolysis or by glucose oxidase. A characteristic increase in reducing power was correlated with the progress of the sugar-amine reaction (10, 32, 34, 35). Several investigators (6, 17, 19, 42) speculated that it could be due to the Amadori rearrangement. If this rearrangement occurred the characteristics demonstrated by the sugar-amine reaction would by explained as those properties were not demonstrated by a

simple N-glycosidic linkage.

The Amadori rearrangement (31, 47) is the isomerization of N-substituted aldosylamines (IV) to 1-amino-1-deoxy-2-ketoses (v). According to Weygand (47) the reaction is acid catalyzed.



Several workers have demonstrated the necessity of the aldehyde and α-hydroxy groups of the glucose molecule (7, 18, 22, 26, 27, 49). However, it was not until recently that Hodge and Rist (25, 26) demonstrated the rearrangement product (V) and its characteristic properties. They demonstrated the rearrangement with both primary and secondary aryl and alkyl amines. The rearrangement occurred spontaneously in the dry state at 25° C. By substituting the C-2 hydroxyl group it was shown that the compound was stable over several years storage at 25° C., and when substituted the compound slowly transformed to a dark brown tarry mass. The Amadori rearrangement product (V) was isolated from this tarry mass in 30 to 50 percent yields. Thus, by blocking the Amadori rearrangement it was demonstrated that browning did not occur. The Amadori rearrangement product, although more stable than the N-substituted

glycosyl amine was heat labile. Upon heating they undergo dehydration and fission to yield colorless reductions and fluorescent substances.

Gottschalk (16) using glucose and phenylalanine and Hodge and Rist (26) with the glycosyl glycine ethyl ester demonstrated the Amadori rearrangement with amino acids. No aldose was recovered upon hydrolysis and the characteristic reducing power was exhibited.

Secondary Reactions in Browning Systems

The formation of furfurals from a glucose-glycine reaction was demonstrated by several investigators (13, 16, 17, 51). Chichester et al. (13) demonstrated 5-hydroxymethyl-2-furfural (HMF) in a glucose-glycine mixture by chromatographic methods. Gottschalk (16) and Gottschalk and Partridge (17) demonstrated the catalysis of furfural formation by amines. Fructose was heated at 100° C. with 2N acetic acid but no HMF was detected. However, upon subjecting the Amadori rearrangement product (V) to these conditions, considerable HMF was formed. Upon heating, the Amadori rearrangement product lost 3 molecules of water to form the Schiff base of HMF. The amine is then liberated by hydrolysis.

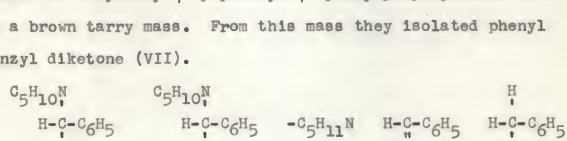
The formation of HMF from the N-substituted-1-deoxy-2-ketose (V) eliminates the sugar radical from the reaction mixture. This would explain why glucose could not be liberated from the browning reaction products by acid or base hydrolysis.

The isolation of the amine portion was accounted for by its hydrolysis from the HMF. This also would account for the fact that glucose may be utilized in greater amounts than the amine in the final stages of the browning reaction.

Wolfrom et al. (50) working with the water soluble, non-dializable portion of a glucose-glycine reaction mixture showed that the methylene carbon of glycine, the No. 1 carbon of glucose, and nitrogen were in a 1 to 1 to 1 ratio in the brown polymer. Elemental analysis indicated that the furfural structure was present but not necessarily in the ring form.

Fragmentation of the sugar moiety in presence of primary amines to highly reactive aldehydes and ketones was demonstrated by Speck (45). They identified pyruvaldehyde and diacetyl in the distillates of several sugar-amine reactions. It is known that amines catalyze the aldol condensation (15, 30). If the reaction was truly reversible it also would be expected to catalyze the reverse or dealdolization.

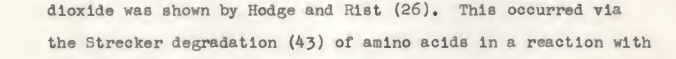
Barker and Cromwell (4) reported the spontaneous decomposition of α-hydroxy-β-piperidyl-β-phenylpropiophenone (VI) to a brown tarry mass. From this mass they isolated phenyl benzyl diketone (VII).



Thus it can be seen that the Amadori rearrangement product may undergo similar decomposition. Hodge and Rist (26) isolated piperidine acetate as the fission product of 1-deoxy-1-piperidino-d-fructose. They postulated that piperidine was split from the radical and the sugar chain was rearranged to yield acetic acid. The piperidine and acetic acid then condensed to form the piperidine acetate which would catalyze the aldol condensation of other sugar fission products.

The formation of reductones from the Amadori rearrangement product (V) upon the loss of 2 molecules of water was demonstrated by Hodge and Rist (26). The reductones were obtained from the N-substituted-1-deoxy-2-ketose either by heating over boiling toluene or storing at 25°C. in the 'dry' state. The reductones browned rapidly in aqueous solution. The rate of browning was increased in the presence of amino acids.

The production of carbon dioxide during the browning reaction has been reported by many investigators including Maillard in his initial experiments. Carbon dioxide production has been shown to parallel aldehyde production (1) and color formation (37). A partial pathway for the liberation of carbon dioxide was shown by Hodge and Rist (26). This occurred via the Strecker degradation (43) of amino acids in a reaction with the dehydroreductones (VIII).



VIII

Schonburg et al. (44) reported that only carbonyl compounds containing the structure,

$$-\overset{O}{\overset{\|}{C}}\left[-C=C\right]_n-\overset{O}{\overset{\|}{C}}-$$

where n equals 0 or an interger, were capable of entering the Strecker degradation. This mechanism would account for the liberation of the amino acid carboxyl group as reported by Maillard.

In recent studies by Stadtman et. al. (46) and Wolfrom et al. (50) it was reported that from 80 to 100 percent of the carbon dioxide liberated was derived from the glycine carboxyl group during the glucose-glycine reaction.

There are several products that can be formed during the browning reaction which would initiate the Strecker degradation. Sugar fission products such as pyruvaldehyde and diacetyl are α-dicarbonyl compounds and would enter the reaction as would the reductones. Hodge and Rist (26) demonstrated the Strecker degradation of dl-α-aminophenylacetic acid with the reductone produced from the Amadori rearrangement product. They identified the corresponding degradation products as benzaldehyde and carbon dioxide. The reaction was carried out using several other amino acids. This reaction would be another source of aldehydes and ketones that may condense and polymerize to form the melanoidin pigments.

Some non-amino acids, which are not active in the Strecker degradation, react more rapidly with sugars forming melanoidins

than the corresponding amino acids (17, 20, 37, 45). Also, Mohammad et al. (40) demonstrated that both proteins and amino acids undergo very rapid browning with acetaldehyde but formaldehyde was an inhibitor for the browning reaction. Since formaldehyde would be formed in the dextrose-glycine reaction it is apparent that the Strecker degradation is not a major color producing reaction.

It readily can be seen that following the sugar-amine reaction the mechanism is very complex. The complexity of the reaction was demonstrated by Chichester et al. (13) when 24 different compounds from a glucose-glycine reaction was separated on a paper chromatogram. Hannan and Lea (20) also demonstrated the complexity by chromatographic methods. During the initial reaction they demonstrated the 1 to 1 condensation product. Upon further reaction time many more compounds were formed.

Browning in Bakery Products

The role of the browning reaction in the baking industry has not been investigated extensively. Haney et al. (18) and Bertram (8) have demonstrated the importance of the Maillard reaction for color formation in bread and sugar cookies. Bertram showed that addition of steam to the oven during the initial baking process enhanced the production of brown pigments. Hlynka and Bass (23) has examined the importance of the browning reaction in the formation of cross linkages in a bread dough.

Haney et al. (18) showed that caramelization was not a major factor in color formation. They replaced sucrose in the

cookie dough with small amounts of dextrose. Significant increases in color occurred with each addition of dextrose up to 5 percent. When added in excess of 5 percent, the color change was very slight thus indicating that 5 percent dextrose saturated the free amino groups with the reducing sugar. The addition of compounds containing free amino groups increased the formation of colored products. Using methylated derivatives of dextrose in model systems and in sugar cookies it was demonstrated that the carbonyl and α-hydroxyl groups of the dextrose molecule were necessary for the production of brown pigments. This confirmed the work of several others and supports the mechanism that Hodge (24) proposed for the Maillard type reaction. The results indicated that the Maillard type reaction was the major factor in the production of the brown pigments in bread and sugar cookies.

An investigation was conducted to find analytical methods for determining the extent of browning in bakery products (18). Fluorometric studies showed that tryptophan and tyrosine were very active in producing substances which fluoresced. The other amino acids present in wheat flour were not as active in the production of fluorscent substances. Absorption curves for amino acid-dextrose systems and bread crust extracts were determined. The model systems and bread crust extracts exhibited only one maxima which occurred between 275 mμ and 285 mμ. Bread crust extracts demonstrated similar absorption characteristics. Although this region is where the furfurals

absorb radiant energy extensively, no free furfural or HMF could be detected in bread crust extracts.

It was observed in this laboratory (18, 48) that sugar cookies containing only sucrose as the added sugar became rancid in a shorter storage period than did cookies prepared using 5 percent dextrose as part of the added sugar. Although this observation had been made, no evidence was available that would indicate the nature of the inhibiting substance(s). The addition of small amounts of reducing sugar initiates the browning reaction and some product or products formed during the course of this reaction may be responsible for the increased stability. Recently Hodge (24) stated the possibility of synthesizing anti-oxidants of reductone character from the sugar-amine reaction. However, no one has demonstrated the fat anti-oxidant properties of the reductones formed during the reaction of amines and reducing sugars. The present work was designed to study and characterize these compounds as related to the stability of sugar cookies during storage.

The observation was made that the color stability of cookies stored in a vacuum pack was greater than when stored in contact with normal atmospheric conditions. The effect of storage conditions upon stability of browned products has not been reported in the literature. Several factors such as gaseous atmosphere, humidity, light, and temperature may influence the color stability. Preliminary experiments (48) have confirmed the observation that cookies in which the browning reaction has occurred

will lose color with storage time. The present investigation was undertaken to study certain atmospheric factors that may influence the loss of color from sugar cookies during storage.

METHODS AND MATERIALS

Cookie Production

Cookies baked for storage tests were of two types and prepared according to the following formula (48):

Ingredient	Percent	Quantity, g.
Flour	100.0	600.0
Sugar*	60.0	360.0
Shortening**	30.0	180.0
Sodium bicarbonate	1.75	10,5
Salt	1.0	6.0
Water	27.	162.0

* Type I cookie, the control, was prepared using 60 percent sucrose. Type II cookie was prepared with 55 percent sucrose and 5 percent dextrose (cerelose brand).

** Primex B and C Shortening[1] was used.

The sugar, shortening, sodium bicarbonate, and salt were creamed at medium speed using the Hobart N-50 mixer. The water was added and the batter mixed until homogeneous. The flour was added and the dough mixed until the flour was incorporated. The cookies were rolled out 6mm in thickness and cut to 59mm in diameter. Baking was at 425° F. for 10 minutes.

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[1] Procter and Gamble, Cincinnati, Ohio.

Storage Studies

The various humidities, under which the cookies were stored, were produced by saturated salt solutions. The saturated salt solutions were placed in the four liter jars used for storage. The cookies were supported above the liquid by a small plastic disk and a heavy piece of aluminum foil. Each group of three cookies was separated by perforated sheets of aluminum foil. The perforations in the aluminum foil allowed adequate circulation.

The relative humidities used in these experiments and the salts employed to prepare the saturated solutions were as follows (2):

Salt	Percent Relative Humidity Produced at 100° F.
Lithium chloride	11.1
Potassium acetate	20.4
Magnesium chloride	31.9
Potassium thiocyanate	41.1
Potassium carbonate	43.4
Sodium dichromate	50.0
Sodium acetate	67.7

An excess of salt was used in each case to insure saturation and prevent possible supersaturation of the solutions.

The 0 percent relative humidity was produced in a desiccator containing calcium chloride. The cookies were stored in the dark at 38° C. Samples were removed at four day intervals for analysis.

Oxygen, carbon dioxide, nitrogen, and air were employed to study the effects of different gaseous atmospheres on cookies during storage. The jars containing the cookies were flushed with the desired gas for five minutes and sealed. Samples were removed for analysis in four day intervals. The gases were replenished at each sampling period.

The odor of the sugar cookies was noted immediately upon opening the container when the samples were removed for analysis.

The pH determinations of the cookies were made according to the procedure described in A.O.A.C. (3) using the Beckman glass electrode pH meter, model H-2.

External color measurements were made with photovolt reflectometer, model 610, using the green tri-stimulus filter (48).

One hundred cookies of each of two types were baked to study the effect of humidity and storage time on color loss in sugar cookies. Sixty cookies of each type were selected that differed no more than one percent reflectance. Ten cookies were assigned randomly to each of six groups. These groups were randomly assigned to a definite humidity. The cookies were removed at definite time intervals and the percent reflectance was determined by two individuals.

The peroxide numbers of the fat contained in the cookies were determined using either acetic acid or citric acid extraction reagent (21). Two 3 gm. samples of cookie, ground in a Hobart grinder, were extracted with 20 ml. acetic or citric acid reagent for two minutes, filtered, and treated with 1 ml.

of a saturated solution of sodium iodide. The samples were allowed to stand in the dark for 15 minutes and diluted with 50 ml. water. Two ml. of one percent starch solution were added and the free iodine titrated immediately with 0.01 N sodium thiosulfate solution.

Isolation and Treatment of Browning Reaction Products

Sugar cookies were prepared as described previously with the exception of the type of shortening added. A shortening containing no anti-oxidant additive was used to replace the Primex B and C Shortening.

A water extract of sugar cookies was prepared by extracting 200 gms. of sugar cookies with 500 ml. water. The extract was prepared by mixing for two minutes in a Waring blender followed by a 15 hour steeping period. The fermentable sugars in the filtrate were removed by yeast fermentation (Saccharomyces cerevisiae). A clear solution was obtained by centrifugation after fermenting for 24 hours. The extracted material was obtained in the dry state by a lyophilization process and stored at -10° F. A bread crust extract was obtained in a similar manner.

The synthetic browning reaction products were produced by heating a 0.2 M glycine and 0.5 M dextrose solution at 85° C. for 24 hours. The solution was a dark brown but no precipitate was present. The final pH of the solution was 4.0. The solids were obtained in the dry state by the lyophilization method

previously described.

A modified Swift keeping quality test was used to determine the presence and relative concentration of fat anti-oxidant substances in the lyophilized extracts. Twenty ml. of lard, containing no added anti-oxidants, was placed in a 20 x 150 mm. test tube with a small quantity of the browning reaction products. The tubes were placed in an oil bath at 121° C. Oxygen was passed through the lard at a constant rate by means of a capillary tube. Organoleptic tests were conducted as well as the determination of peroxide content.

The quantitative determination of reducing groups were made by the Chapman-McFarlane ferricyanide test (12) as modified by Hlynka and Bass (23). This test was designed to determine the reducing substances formed during the browning reaction.

The 2, 6-dichlorophenolindophenol was prepared and purified by the method described by Bessey and King (9). The reducing power was determined in an alkaline solution (26). Five drops 20 percent sodium hydroxide and 2 drops 2, 6-dichlorophenolindophenol reagent (9) were added to 5 cc. of solution containing the lyophilized extracts. The solutions were checked visually for the rapidity of decolorization of the blue dye. Additional reagent was added if initial quantity was decolorized. The tests were carried out at room temperature.

The oxidation of the enediol structure by o-dinitrobenezene was performed by the method of Fearon and Kawerau (14).

The reaction of iodine with the browning reaction products was carried out in an acid media (26). Two-hundred-fifty mg. of the lyophilized extracts in 25 cc. of 10 percent acetic acid was titrated at room temperature with a standard iodine solution. Two ml. of one percent starch solution were added as an indicator. The titration was continued until the blue color was stable for 1 minute.

EXPERIMENTAL RESULTS AND DISCUSSION

Two types of sugar cookies were baked. The sucrose cookie, containing 60 percent sucrose, did not brown noticeably. The formula did not include dry milk solids and eggs which contain reducing sugars and proteins that would initiate the browning reaction. Consequently, the only reducing sugars available was the very small quantities present in the flour (29). However, the dextrose cookie, containing 55 percent sucrose and 5 percent dextrose as the added sugars, browned very markedly. Thus, excellent conditions were produced for studying the browning reaction in baked products. The sucrose cookie was the control and the effects of the browning was studied using the dextrose cookies.

Storage Studies

The study of the effect of relative humidity and storage time on the hydrogen-ion concentration of sugar cookies is presented in Tables 1 and 2 in the appendix. Moisture content and

storage time had no significant effect on the hydrogen-ion concentration. These results indicated that the hydrolysis of fat was negligible. Thus, it may be concluded that the moisture content had no apparent effect on hydrolytic rancidity in sugar cookies.

Peroxides numbers have been used to follow oxidation of fats. In an attempt to obtain quantitative data on the oxidative changes of the fat in sugar cookies during storage and to correlate such changes with organoleptic tests the data in Tables 3 and 4 were collected. Unfortunately these data were erratic and no definite trend was established even though certain samples were known to be rancid as shown by organoleptic testing.

The effect of moisture content and storage time on the odor of sugar cookies is presented in Tables 1 and 2. A definite relationship between humidity and time required for a rancid condition to develop was established for each type of cookie.

Table 1. Effect of moisture content and storage time on the odor of sucrose cookies.

Relative Humidity	Moisture Content	Time to Rancid Conditions
%	%	days
11.1	3.40	64
20.4	4.40	56
31.9	5.05	44
41.1	5.20	40
50.0	5.40	36
67.7	6.15	24

Table 2. Effect of moisture content and storage time on the odor of dextrose cookies.

Relative Humidity	Moisture Content	Time to Rancid Conditions
%	%	days
11.1	3.65	96
20.4	4.30	72
31.9	5.25	56
41.1	5.45	56
50.0	5.65	52
67.7	6.75	40

For the sucrose cookie organoleptic rancidity developed in 24 days when stored in an atmosphere having a relative humidity of 67.7 percent. At a relative humidity of 11.1 percent rancidity was not detected until 64 days. The moisture content of these cookies was 6.15 percent and 3.40 percent, respectively. This illustrates the tremendous effect of moisture content on sugar cookie stability when stored under otherwise equivalent conditions.

The dextrose cookies showed the same trends as did the sucrose cookies. Thus, moisture accelerated oxidative rancidity in the range which was studied. The use of 5 percent dextrose in the sugar cookies retarded the onset of rancidity. The cookies stored at the highest humidity had an increased stability of approximately 70 percent. This confirmed preliminary work carried out in this laboratory (18, 48).

The anti-oxidant effect was observed at all moisture contents. These results suggest that some product(s) formed during the browning reaction has the properties to inhibit oxidative rancidity in sugar cookies.

The effect of moisture and storage time on the percent reflectance are presented in Plate I. Their increase in percent reflectance as a function of the storage period for each humidity was analyzed statistically by methods presented by Box (11).

A large loss of color was noted in the dextrose cookies after 10 days of storage with the loss of color being greatest in the high humidity. With the exception of the cookies stored at 20.4 percent relative humidity, the extent of color fading corresponded directly to the relative humidity in which they were stored. A similar corresponding loss was noted at 26 days. The change in color after 26 days was negligible.

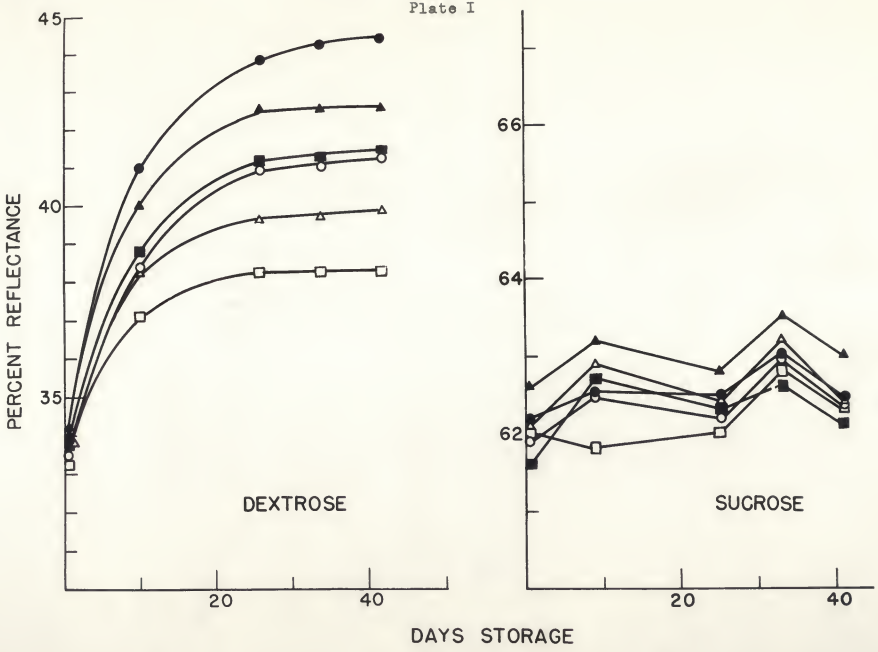
The statistical analysis indicated the mean daily growth rates for the full 42 days were highly significantly different from one group to the next. It was also demonstrated that the shapes of the growth curves were significantly different with the exception of the 20.4 percent and 31.9 percent humidity groups.

The cookies containing only sucrose as the added sugar did not show an appreciable change in color. These results were to be expected because use of a non-reducing sugar did not initiate the browning reaction. Hence, there were no dark pigments to be altered during storage. The statistical analysis demonstrated that there were no significant differences in color loss between the humidity groups and there was no significant change in color for the entire storage period.

Plate I

Effect of relative humidity and storage time on the percent reflectance of sugar cookies. ●-67.7 R.H., ▲-43.4% R.H., O-31.9% R.H., ■-20.4% R.H., △-11.1% R.H., and □-0% R.H.

Plate I


45
40
35
PERCENT REFLECTANCE
DEXTROSE
20
40
66
64
62
SUCROSE
20
40
DAYS STORAGE

The effect of gaseous atmosphere and storage time on the peroxide numbers are presented in Tables 5 and 6 in the appendix. The value of these data was questionable as no definite trends could be established although the samples were known to be rancid. Organoleptic testing for rancidity showed no effect of gaseous atmosphere on the development of oxidative rancidity (Table 3). Mukherjee et al. (41) have stated that oxygen dissolved or entrained in fatty materials may be sufficient to produce a rancid condition. More rigorous methods should be used to eliminate these factors.

Table 3. Effect of gaseous atmosphere and storage time on the odor of sugar cookies.

Atmosphere	Time to a Rancid Condition	
	Sucrose Cookie	Dextrose Cookie
	days	days
Air	60	100
Oxygen	60	100
Carbon Dioxide	60	108
Nitrogen	60	108

The effect of gaseous atmosphere and storage time on the color loss in sugar cookies are presented in Tables 7 and 8 in the appendix. These data indicate that type of gaseous atmosphere had no significant effect on color stability of either type of sugar cookie.

Characterization of the Reducing Components of Browning Reaction Systems

It was established in the storage studies that the addition of dextrose to sugar cookies increased the stability of fat to

oxidative rancidity. It was believed that this desired characteristic was due to the products of a Maillard type browning reaction. In the course of a sugar-amine reaction Hodge and Rist (26) isolated a compound of reductone character. These compounds are characterized in particular by the enediol structure which may be readily oxidized or reduced. In view of the relationship between the two systems, studies were initiated to test for the presence and concentration of the reductones and their relation to fat stability in an isolated system.

The application of the Swift keeping quality test for determination of the effects of cookie extracts on lard is shown in Plate II. The samples were considered rancid at a peroxide number of 8. This value was determined by organoleptic testing.

The lyophilized water extract of the sucrose sugar cookies exhibited weak anti-oxidant properties. The addition of 0.2 percent and 1.0 percent extracts exhibited increasing fat stability although the change was small. A similar lyophilized extract of the dextrose sugar cookie demonstrated considerably greater anti-oxidants properties. The increase in fat stability was shown to be related to the amount of cookie extract added to the lard.

The inhibition of the development of rancidity in fat by synthetic browning reaction products and butylated hydroxy anisole are shown in Plate III. The stability of fat was increased considerably by addition of 0.01 percent synthetic browning reaction products. The addition of 0.1 percent and 0.2 percent

exhibited greater anti-oxidant properties. There was an increase of approximately 40 percent in the fat stability when 0.2 percent synthetic browning reaction products were added. Butylated hydroxy anisole gave a similar type of curve as did the browning reaction products. The addition of 0.005 percent exhibited greater anti-oxidant power than 0.2 percent of the synthetic browning reaction products.

The effects of dextrose and bread crust extract on fat stability are shown in Table 4. The dextrose exhibited no appreciable effect on the fat stability. Similarly, bread crust extract exhibited no effect on the fat stability. These results do not appear tenable at the present in view of the fact that non-fermentable reducing compounds should also be present in bread crust as a result of the browning reaction.

Table 4. Effect of anhydrous dextrose and bread crust extracts on fat stability.

Time	Peroxide Numbers		
	1*	2*	3*
hrs.	MmO_2	MmO_2	MmO_2
0	-	-	-
3	.88	.90	
3½			.95
4	1.00	1.30	
4½			1.91
5	2.52	2.17	
5½	6.45	4.08	4.42
6	11.83	16.90	13.51

* 1 - Standard-no additives
2 - 0.2 percent anhydrous dextrose
3 - 0.5 percent bread crust extract

Plate II

Effect of cookie extracts on the stability of fat. ●-standard, 0-0.2% extract, ■-0.6% extract, and Δ-1.0% extract.

Plate II

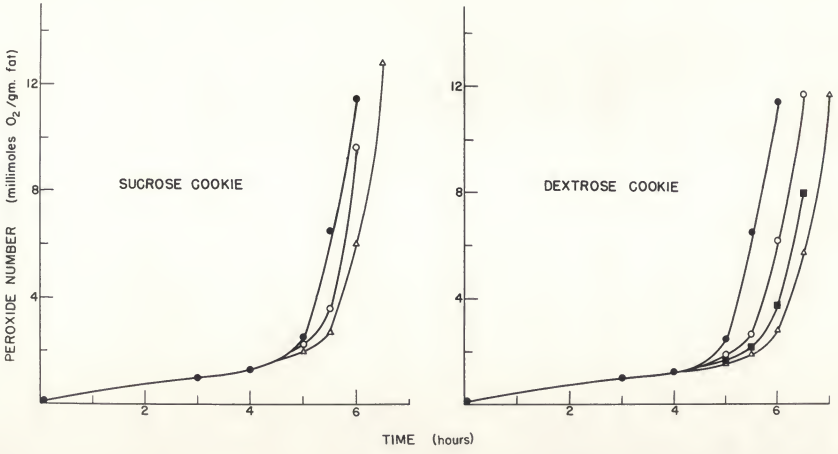
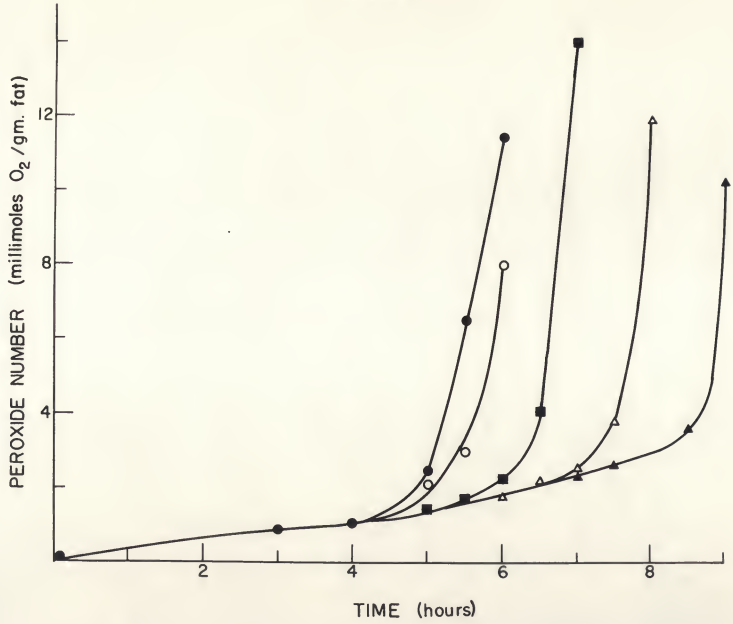

PEROXIDE NUMBER (millimoles O_2/gm. fat)
12
8
4
SUCROSE COOKIE
2
4
6
DEXTROSE COOKIE
TIME (hours)

Plate III

Effect of synthetic browning reaction products and butylated hydroxy anisole on stability of fat. ●-standard, 0-0.01% browning reaction products (BRP), ■-0.1% B.R.P., △-0.2% B.R.P., and ▲-0.005% butylated hydroxy anisole.

Plate III



The results of the Chapman-McFarlane test are shown in Table 5. The results showed the presence of reducing compounds. It was of interest that the extract from sucrose cookies had but a small amount of reducing groups while the dextrose cookies and the dextrose-glycine system showed an appreciable amount. It was evident also that there was a relationship between the concentration of reducing groups and the stability imparted to the fat to oxidative rancidity as shown in Plates II and III.

Table 5. The reducing properties of synthetic reaction products and sugar cookies extracts.

Reducing Test	Synthetic Browning Reaction Products	Dextrose Cookie Extract	Sucrose Cookie Extract
Chapman-McFarlane ferricyanide (moles reducing groups x 10^{-5}/gm)	72	26.4	6.3
o-dinitrobenzene	violet	violet	no color
2,6-dichlorophenol-indophenol	rapid decolorization	rapid decolorization	very slow decolorization
Reaction with iodine (moles $I_2 x 10^{-5}$/gm)	7.04	3.71	2.24

The small amount of reducing groups found in sucrose cookies was correlated with the lack of stability of these cookies to storage. The slight inhibition of rancidity in the sucrose cookies may be due to a small amount of browning that resulted from the presence of traces of reducing sugar in the flour. Natural anti-oxidants in the flour also may account for the

limited stability of the sucrose cookies. The dextrose cookie extract contained 4 times more reducing groups than did the sucrose cookie extract. This increase in reducing groups was due to the products of the browning reaction.

Further characterization of the reducing properties of the dextrose cookie extract was made by use of 2,6-dichlorophenolindophenol and o-dinitrobenzene (Table 5). It was shown that synthetic browning reaction products and dextrose cookie extract reduced 2,6-dichlorophenolindophenol rapidly and the reducing groups in sucrose cookie extract reacted very slowly. Evidence for the presence of the enediol structure in the browning reaction products was obtained by use of o-dinitrobenzene. Synthetic browning reaction products and dextrose cookie extracts gave positive tests. The test was negative for the sucrose cookie extract. This indicated that reductone like compounds were formed during the browning reaction while no such compounds were formed in the sucrose cookie.

The reaction of iodine and browning reaction products was demonstrated (Table 5). It was shown that some product(s) produced during the browning reaction have the ability to reduce, add, or react in some manner with the iodine. The course of the reaction was not clear. The sucrose cookie extract reacted with an appreciable quantity of iodine even though very little browning occurred. The dextrose cookie extract reacted with a considerably larger quantity of iodine indicating that the browning reaction products formed in sugar cookies do react with

iodine in some manner. The quantity of iodine which reacted appears to be related to the concentration of reducing groups. Since 1 mole of reductone will react with two of iodine, these results support the postulate that reductones are formed during the browning reaction.

The data in Table 5 indicates that reducing groups were produced in a sugar cookie during the formation of the brown melanoidin pigments. The reducing groups are similar to those produced in a dextrose-glycine reaction mixture. In the absence of reducing sugars the reducing groups were not formed. The chemical nature of the reducing compounds indicate that they contain the enediol structure and may be classified as a true reductone (26). These results corraborate those of Hodge and Rist (26).

The concentration of fat anti-oxidants in the water extracts of the dextrose sugar cookies was not great, particularly, when compared to the efficiency of the butylated hydroxy anisole to inhibit oxidative rancidity. This might be expected in view of the fact that perhaps not all reducing compounds were extracted from the cookie and also due to the transitory nature of reductones in the browning reaction. Nevertheless, their concentration in the dextrose cookie appears to be sufficient to impart significant fat anti-oxidant effects, thus, increasing the shelf life of the cookies.

SUMMARY

An investigation was conducted on the factors and conditions affecting storage stability of sugar cookies.

1. The type of gaseous atmosphere had no apparent effect on the storage stability of sugar cookies.

2. The storage stability of sugar cookies to oxidative rancidity was shown to be related to the moisture content. The moisture exerted a catalytic effect on the development of rancidity in sugar cookies.

3. The addition of 5 percent dextrose to sugar cookies increased their stability to oxidative rancidity at all moisture levels studied.

4. The peroxide number determinations failed to give an indication of oxidative rancidity.

5. Hydrolytic rancidity was not a major factor in the development of a rancid condition in sugar cookies.

6. Cookies prepared with 5 percent dextrose tends to fade with storage time. The color loss was a function of moisture content. Cookies stored with a high moisture content lose color at a greater rate than cookies stored with low moisture contents.

7. The use of lyophilized water extracts of sugar cookies indicated that fat anti-oxidants were formed during the browning reaction. These anti-oxidants were similar to those produced by a dextrose-glycine reaction.

8. Characterization of the reducing compounds indicated they contained the enediol structure and were classified as true

reductones.

9. The concentration of the reductones in the dextrose cookie extract was not great. This might be due to the transitory nature of these substances and possibly all were not extracted from the cookies. However, the concentration was great enough to impart significant anti-oxidant effects in the dextrose cookie.

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APPENDIX

Suggestions for Future Study

The work concerning the effect of various gaseous atmospheres on the storage stability of sugar cookies should be repeated. The techniques used to produce inert atmospheres should be improved and thus, eliminate the effect of the very small quantities of oxygen remaining in the atmosphere and in the cookies.

The development of new chemical methods to follow fat oxidation in the sugar cookies is necessary. These tests are of value when supporting organoleptic testing for the development of rancidity.

Fundamental approaches to the problem of degradation of the brown polymers with time is necessary. This information may be beneficial to stabilize the brown color of food products. Also, it is necessary to elucidate the mechanism or mechanisms involved when browning occurs. Chromatographic techniques should be helpful in this respect. The many products that are formed during this reaction should be identified. These fundamental approaches are necessary in order to control the browning reaction.

The elucidation of the properties and syntheses of the reductones formed during the browning reaction may be useful in the fat industry. Possibly, some very useful anti-oxidants may be developed.

Table 1. Effect of moisture content and storage time on the hydrogen-ion concentration (pH) of sucrose sugar cookies.

Storage Time : Humidity (%)	11.1	20.4	31.9	41.1	50.0	67.7
: Moisture (%)	3.40	4.40	5.05	5.20	5.40	6.15
days	pH	pH	pH	pH	pH	pH
0	9.4	9.6	9.6	9.6	9.6	9.4
8	9.7	9.7	9.7	9.7	9.8	9.7
16	9.8	9.8	9.8	9.8	9.7	9.7
24	9.8	10.0	9.9	9.9	9.8	9.7
32	10.0	9.9	9.8	9.9	9.8	9.7
40	9.8	9.8	9.7	9.7	9.6	9.6
56	9.5	9.5	9.6	9.5	9.5	9.3

Table 2. Effect of moisture content and storage time on the hydrogen-ion concentration (pH) of dextrose sugar cookies.

Storage Time : Humidity (%)	11.1	20.4	31.9	41.1	50.0	67.7
: Moisture (%)	3.65	4.30	5.25	5.45	5.65	6.75
days	pH	pH	pH	pH	pH	pH
0	8.3	8.3	8.4	8.3	8.2	8.2
8	8.4	8.4	8.7	8.3	8.6	8.7
16	8.8	8.6	8.6	8.6	8.8	9.1
24	8.8	8.6	9.0	8.9	8.8	9.1
32	8.4	8.9	8.6	8.7	8.4	8.2
40	8.0	8.5	8.1	8.1	8.2	8.2
56	7.8	8.0	8.2	8.0	7.9	7.7

Table 3. Effect of moisture content and storage time on the peroxide number of sucrose sugar cookies. *

Storage Time : Humidity (%) : Moisture (%)	11.1 3.40	20.4 4.40	31.9 5.05	41.1 5.20	50.0 5.40	67.7 6.15
days	MMO_2	MMO_2	MMO_2	MMO_2	MMO_2	MMO_2
0	1.22	1.43	1.44	1.22	1.31	1.57
4	1.89	1.60	1.68	1.57	1.48	1.79
8	1.73	1.40	1.75	1.56	1.39	1.80
12	1.90	1.52	1.55	1.43	1.49	1.99
16	2.53	2.54	2.01	2.25	2.63	2.49
20	2.01	2.53	2.39	2.66	2.46	2.58
24	3.50	3.27	3.22	4.05	3.62	3.01
28	2.91	2.30	2.56	2.56	3.08	3.08
32	2.46	2.56	3.29	3.32	3.36	2.66
36	2.68	2.46	2.58	2.87	3.08	2.84
40	2.72	2.60	2.17	2.08	3.26	3.28
44	2.77	2.46	2.53	2.88	2.88	.66
56	.87	.87	.73	.73	.78	.83
64	.71	.50	.52	.45	.45	.61
80	.97	.97	.69	.73	.76	.87
88	.97	.75	.62	.62	.61	.73
96	1.11	.87	.78			
104	1.16	.95	.66			
112	1.29	1.01				

*Acetic acid reagent was used for the extraction of perioxide from 0 days to 44 days. From 56 days to 112 days storage citric acid reagent was used.

Table 4. Effect of moisture content and storage time on the peroxide number of dextrose sugar cookies.*

Storage : Humidity (%)	11.1	20.4	31.9	41.1	50.0	67.7
Time : Moisture (%)	3.65	4.30	5.25	5.45	5.65	6.75
Days	MMO_2	MMO_2	MMO_2	MMO_2	MMO_2	MMO_2
0	1.10	1.21	1.01	1.03	1.10	1.13
4	.83	1.10	..88	.97	.75	1.14
8	.90	1.00	.79	.97	.53	1.12
12	.90	1.17	.93	.97	1.10	1.64
16	1.61	1.90	1.55	1.73	1.90	1.62
20	1.85	1.73	1.55	2.14	1.28	2.42
24	1.43	1.62	1.62	2.25	2.58	2.01
28	1.52	1.83	1.29	2.23	2.42	2.49
32	2.04	1.87	1.92	2.28	3.08	3.32
36	2.16	1.83	2.32	3.31	3.36	2.85
40	1.53	2.01	1.80	2.01	2.29	1.65
44	1.61	1.42	2.43	2.01	1.61	1.94
56	.36	.59	.40	.52	.55	.59
64	.35	.43	.33	.35	.49	.45
80	.38	.41	.45	.49	.47	.50
88	.28	.31	.28	.33	.33	.57
96	.35	.42	.31			
104	.42	.42	.43			
112	.38	.38				

*Acetic acid reagent was used for the extraction of peroxide from 0 days to 44 days. From 56 days to 112 days storage. Citric acid reagent was used.

Table 5. Effect of gaseous atmosphere and storage time on the peroxide number of sucrose sugar cookies.

Storage Time	Type Atmosphere : Moisture (%)	Air 4.80	Oxygen 5.10	Carbon Dioxide 5.35	Nitrogen 5.15
Days		MMO_2	MMO_2	MMO_2	MMO_2
0		1.24	1.24	1.52	1.52
4		1.84	1.76	1.68	1.75
8		2.61	2.56	2.28	3.01
12		2.29	2.18	2.56	2.11
16		2.43	2.25	2.32	2.70
28		.61	.66	.62	.66
36		.52	.48	.54	.52
52		.73	.64	.45	.49
60		.42	.45	.38	.42
68		.50	.50	.47	.50
76		.55	.57	.52	.52
84		.57	.62	.49	.59
92		.47	.52	.40	.55
100		.68	.62	.62	.69
108		.59	.57	.47	.59
116		.66	.69	.55	.62

*Acetic acid reagent was used for the extraction of peroxides from 0 to 16 days. From 28 to 116 days storage time citric acid reagent was used.

Table 6. Effect of gaseous atmosphere and storage time on the peroxide number of dextrose sugar cookies.*

Storage Time	Type Atmosphere Moisture (%)	Air 4.35	Oxygen 4.40	Carbon Dioxide 4.50	Nitrogen 4.45
Days		MMO_2	MMO_2	MMO_2	MMO_2
0		1.10	1.10	1.21	1.21
4		1.54	1.81	1.69	1.73
8		1.71	1.38	1.55	1.38
12		1.01	1.73	1.46	1.49
16		.83	1.45	1.14	1.44
28		.31	.43	.43	.45
36		.49	.54	.35	.26
52		.31	.37	.26	.17
60		.21	.29	.19	.21
68		.38	.38	.28	.38
76		.35	.35	.31	.31
84		.35	.35	.38	.38
92		.45	.36	.38	.43
100		.49	.42	.40	.40
108		.35	.36	.35	.36
116		.35	.35	.24	.24

*Acetic acid reagent was used for the extraction of peroxides from 0 to 16 days. From 28 to 116 days storage time citric acid reagent was used.

Table 7. Effect of gaseous atmospheres and storage time on the apparent luminous reflectance of sucrose sugar cookies.

Storage Time	Gaseous Atmosphere			
	Air	Oxygen	Carbon Dioxide	Nitrogen
Days	%	%	%	%
0	60.5	59.9	58.3	57.9
8	60.7	59.0	57.5	57.8
16	59.8	58.6	57.5	57.4
24	59.0	58.2	57.2	57.3
32	59.3	57.9	52.1	57.3
40	58.5	57.8	56.2	57.0
48	58.4	57.3	56.4	56.5
56	58.6	57.0	57.0	56.6

Table 8. Effect of gaseous atmosphere and storage time on the apparent luminous reflectance of dextrose sugar cookies.

Storage Time	Gaseous Atmospheres			
	Air	Oxygen	Carbon Dioxide	Nitrogen
Days	%	%	%	%
0	29.5	33.3	28.2	31.2
8	30.3	33.0	28.7	31.4
16	30.0	32.9	28.1	30.1
29	30.8	34.1	29.4	31.5
32	30.8	34.1	28.8	31.8
40	31.2	34.2	29.2	31.6
48	30.8	34.5	28.8	31.3
56	31.0	33.9	28.7	31.0

THE EFFECT OF THE BROWNING REACTION ON THE STABILITY OF STORED SUGAR COOKIES

by

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B. S. Kansas State College
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An investigation was conducted on the effect of atmospheric conditions on the storage stability of sugar cookies and the role of the browning reaction products on fat stability in sugar cookies. Two types of sugar cookies were used in this study. Cookies prepared using 60 percent sucrose did not brown noticeably. When 5 percent of the sucrose was replaced with dextrose, a considerable amount of brown melanoidin pigments were formed in the sugar cookies.

The effect of type of gaseous atmosphere had no apparent effect on the storage stability of the sugar cookies during the period studied.

Hydrolytic rancidity was not a major factor in the development of a rancid condition in the sugar cookies.

The storage stability of sugar cookies to oxidative rancidity was shown to be related to the moisture content. The moisture exerted a catalytic effect on the development of rancidity in sugar cookies. However, the addition of 5 percent dextrose to the sugar cookies increased their stability to oxidative rancidity at all moisture levels studied.

The color of sugar cookies prepared with 5 percent dextrose tends to fade with storage time. The color loss was a function of the moisture content and time. Cookies stored with high moisture contents lose color at a greater rate than do cookies stored with low moisture contents.

Lyophilized water extracts of sugar cookies and a dextrose-glycine reaction mixture exhibited definite fat anti-oxidant

properties. This was demonstrated by use of a modified Swift keeping quality test. The dextrose cookie extract and the dextrose-glycine reaction products exhibited considerably greater anti-oxidant properties than did the extract of cookies prepared with only sucrose. Quantitative determination of reducing groups formed during the browning reaction correlated very well with the fat anti-oxidant properties of the extracts. The anti-oxidant compounds formed during the browning reaction exhibited reductone characteristics.

The concentration of the reducing groups formed in the cookies during the browning reaction was not great. This may be due to the transitory nature of these substances and also it is possible that not all the reducing material was extracted from the cookies. However, their concentration appears to be great enough to account for a significant increase in the shelf life of the sugar cookies.