Effects of Moisture Content on the Maillard Browning Model System upon Microwave Irradiation

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Browning intensities of an L-cysteine/D-glucose model system with different moisture contents (0–40%) upon microwave irradiation for 2.5 min at the high setting of a 700-W microwave oven were measured by a UV spectrophotometer at 420 nm. The volatile compounds generated were analyzed by gas chromatography and mass spectrometry. Maximum browning intensity occurred at approximately 14% moisture. The effects of irradiation time for each of the moisture contents (14, 22, and 26%) were also investigated. For these moisture contents, browning increased with irradiation time until reaching a plateau at 2.5 min of irradiation. The moisture content appeared to determine the browning intensity at the initial stage of exposure to microwave irradiation. The maximum number of volatiles was produced at 11% moisture. Major compounds obtained from this model system were 2-thiophenethiol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, and 2-acetylfuran.

INTRODUCTION

Foods prepared by using a microwave oven usually generate less desirable flavors and browning (Risch, 1989) than those prepared by a conventional oven. MacLeod and Coppock (1976) found that the amount of volatiles obtained from microwave-boiled beef was one-third that of beef prepared conventionally. In another study, microwave-prepared beef samples were weaker in flavor and less pleasant than samples prepared by conventional methods (Brodero et al., 1980). Microwave-baked bread produced poorer sensory scores (Lorenz et al., 1973) and microwave-baked cake generated different chemical profiles (Whorton and Reineccius, 1989) compared to those prepared conventionally.

The differences in the flavors produced by microwave irradiation and conventional heating are due to their heating characteristics. The high temperature of the surroundings in a conventional oven causes the Maillard reaction, leading to surface browning and production of desirable flavors in foodstuffs. Similar browning and flavor production, however, do not occur in foodstuffs prepared by microwave ovens partly because the surroundings of the oven do not heat to a high temperature. In addition, microwave irradiation causes the evaporation of water molecules from the food system into the low-temperature surroundings in the microwave oven, resulting in the lack of crispiness in foodstuffs. The extent to which food systems heat in a microwave oven is dependent on the amount of polar molecules (such as water) in the system.

Some studies involving moisture content during microwave treatment include its effects on enzyme inactivation (Abara and Hill, 1981) and flavors in cooked cabbage (MacLeod and MacLeod, 1970). However, more studies are needed on the effects of moisture content on both the degree of browning and the production of flavors during microwave irradiation.

This study attempts to establish a basic understanding of the relationship during microwave heating between moisture content on the one hand and flavor production and browning intensity on the other. The Maillard model system, consisting of L-cysteine and D-glucose, was used in this investigation.

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EXPERIMENTAL PROCEDURES

Materials. L-Cysteine and D-glucose were purchased from Aldrich Chemical Co. (Milwaukee, WI); dichloromethane was obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ). The stock solution of internal standard for GC analysis was prepared by adding 1 mg of undecane to 10 mL of dichloromethane and was stored at 5 °C.

Sample Preparation. Preweighed Pyrex dishes, each containing L-cysteine (12.5 mmol) and D-glucose (12.5 mmol), were used as the Maillard model mixture. The final weights were measured to obtain the weights of the solid mixtures in each dish. The moisture in the solid mixtures was obtained according to the procedure described by Bosin and Easthouse (1970). The solid mixtures were placed in the upper level of a desiccator; a Pyrex dish containing 100 mL of deionized water was placed in the lower level. The temperature of samples during equilibration was monitored by inserting a thermometer into the chamber. The temperature throughout the experiments was at 25 ± 1 °C. The water was stirred constantly to shorten the exposure time of the solid mixtures to moisture to avoid browning reactions. At various time intervals, the Maillard mixture was removed and weighed. The amount of water introduced was determined by calculating weight differences. The resulting mixture was then stirred into a slurry. Control samples (without moisture) were microwaved immediately after initial weighing.

The slurry was transferred into an Erlenmeyer flask and microwaved for 2.5 min at the high setting of a 700-W microwave oven. After irradiation, each paste was dissolved in 100 mL of deionized water. The samples were prepared in open systems to mimic actual cooking conditions. Five milliliters of each sample was used for absorbance measurements. After a 1:5 dilution was made, the degree of browning in the sample was determined at 420 nm.

The remaining 95 mL was adjusted to pH 8 with 6 N NaOH to enhance the extraction efficiency of nitrogen-containing heterocyclic compounds. The microwave products were extracted with 50 mL of dichloromethane with a liquid–liquid continuous extractor for 6 h, and the extract was dried over anhydrous sodium sulfate for 12 h. Sodium sulfate was then removed by filtration, and the filtrate was concentrated to slightly in excess of 1 mL by fractional distillation with a Vigreux column. The solution was then transferred into a concentration tube and its volume reduced to exactly 1 mL under a purified nitrogen stream. Undecane (0.5 mL of stock solution) was then added as a gas chromatographic internal standard, and the solution was further reduced to 0.2 mL under a nitrogen stream.

The effects of irradiation time on the browning intensity at various moisture contents were also studied. The model mixtures were equilibrated to 14, 22, and 26% moisture contents according

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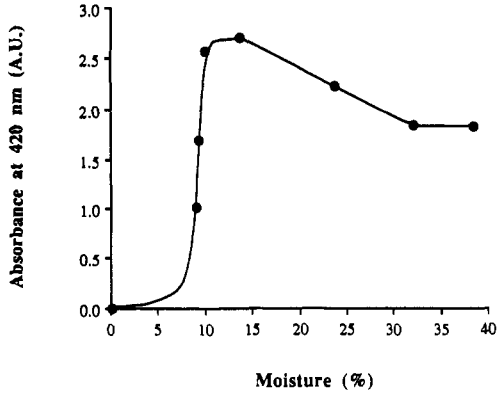

Figure 1. Browning intensity of the L-cysteine/D-glucose model system as a function of moisture content upon 2.5 min of microwave irradiation.

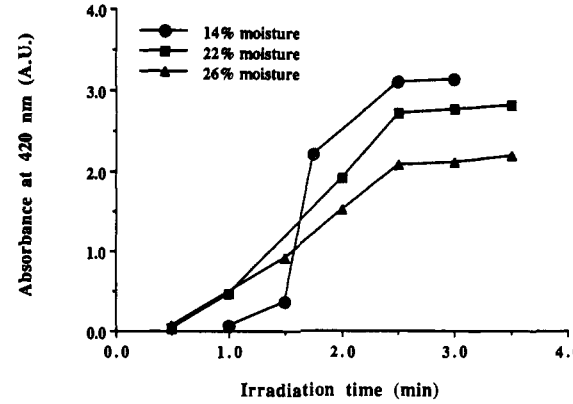

Figure 2. Browning intensity of the L-cysteine/D-glucose model system as a function of irradiation times for samples with different moisture contents.

to the procedure described above. The mixtures at each of the moisture contents were then irradiated at the high setting of a 700-W microwave oven for up to 3.5 min. All data were obtained in duplicate.

Identification of Products Formed in the L-Cysteine/D-Glucose Model System. The samples were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Identification of the chromatographic peaks of the samples was made by comparing their mass spectra and gas chromatographic retention indices to those of authentic compounds.

Instruments. A Quasar Model MQ 7796 AW, 700-W, Easy-Matic Cooking microwave oven was used for the irradiation of the samples.

A Hewlett-Packard (HP) Model 8452A diode array spectrophotometer with HP 89510 UV-vis software was used to measure the degree of browning at 420 nm.

An HP Model 5890 gas chromatograph equipped with a flame ionization detector (FID) and a 60 m × 0.25 mm i.d. × 0.2 μm df DB-Wax bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA) was used for routine analysis. Peak areas were integrated by using a Spectra Physics Chromjet integrator. The GC oven was held at 60 °C for 4 min, programmed at 4 °C/min to 180 °C, and then held for 30 min. The temperatures of the injector and the detector were 240 and 250 °C, respectively. The linear velocity of the helium carrier gas flow was 25.5 cm/s.

An HP Model 5890 GC interfaced to a VG Trio II mass spectrometer with a VG 11-250 computer data system was used for MS identification of the GC components. The ionization voltage was 70 eV, and the ion source temperature was 150 °C. The column and oven conditions for GC/MS were as described for the HP 5890 GC/FID analysis.

RESULTS AND DISCUSSION

Figure 1 shows the browning intensity of the model mixtures at various moisture contents after microwave irradiation for 2.5 min. The mixtures with no moisture (control) did not show any browning after as much as 6 min of microwave exposure. The weight of the mixture decreased with irradiation time until remaining constant after 4 min of exposure. The solid mixture did not form any "crust" that may trap water (Troller and Christian, 1978). Therefore, the weight loss corresponded to the removal of water from the mixture, which amounted to 0.1%. The lack of browning in the control samples after microwave irradiation was probably due to small amounts of polarizable water molecules available for microwave absorption. In addition, there is also a lack of water to serve as an aqueous reaction medium.

The browning intensity increased with moisture content and reached a maximum intensity at approximately 14%, after which point the intensity started to decline with increasing moisture content. The decline in browning intensity observed may be due to a dilution of the sample as the moisture increased (Eicher and Karel, 1972). An increase in moisture content lowers the rate of Maillard browning caused by dilution of its starting material.

The region where browning increased rapidly with a small change in moisture content, termed the threshold level, occurred between 10 and 14% moisture content. The presence of polarizable molecules available for microwave absorption may have contributed to the initial increase in browning intensity. The trend observed in this region suggests that adequate moisture acted as a reaction medium to increase the rotational mobility of the precursors, which consequently results in the absorption of microwave energy. However, this range of moisture content was not in sufficient excess to cause the inhibition of the forward Maillard reaction, in particular the dehydration step in the formation of the Schiff base.

Figure 2 shows the effects of irradiation time on microwave browning at various moisture contents. Browning increased with irradiation time and plateaued after 2.5 min. After only 1 min of irradiation, samples at 14% moisture content did not brown significantly; absorbance at 420 nm was 0.069 AU. However, samples at 22% moisture content showed significantly browning after 1 min of irradiation, with an absorbance of 0.464 AU. This suggests that at the initial stage of microwave irradiation, water plays a crucial role in browning intensity. This finding may be due to the dielectric properties of the model system at various moisture contents. At the initial stage of irradiation, the source of energy is solely or predominantly due to microwave irradiation, as there are more polarizable dipoles (such as water) to undergo rotation and absorb microwave energy. However, as the irradiation proceeds, the source of energy is probably due to microwave and thermal effects. In addition, as the irradiation proceeds, water is removed from the system. This dehydration process favors the formation of brown color in the model system.

The trend observed in Figure 2 may be divided into two regions. In the region before maximum browning is obtained for each moisture content, the change in absorbance increases rapidly over a short period of irradiation time. This is clearly demonstrated in samples with 14% moisture. A small change in the irradiation time (i.e., between 1.5 and 1.75 min) causes the sharpest change in the browning intensity. Therefore, to achieve a browning intensity less than the maximum, an exact irradiation time must be used.

In the second region, where the maximum browning is reached (greater than 2.5 min), the change in the browning

Table I. Amount of Total Volatiles Generated at Various Moisture Contents from an L-Cysteine/D-Glucose Model System upon 2.5 min of Microwave Irradiation

moisture content, %	total volatiles (GC peak area ratio)[a]	moisture content, %	total volatiles (GC peak area ratio)[a]
9	5.1	24	8.2
11	11.1	30	5.9
14	8.6	32	5.4

[a] GC peak area of total volatiles divided by GC peak area of internal standard.

Table II. Compounds Identified in an L-Cysteine/D-Glucose Model System at Various Moisture Contents upon 2.5 min of Microwave Irradiation

compd	GC peak area ratio[a] at moisture content of 9%	11%	14%	24%	30%	32%
2-methylpyridine	b	b	b	0.01	0.01	0.01
thiazole	0.02	0.03	0.05	0.01	0.01	0.01
2-furaldehyde	0.06	0.10	0.05	0.04	0.04	0.04
2-acetylfuran	0.08	0.16	0.36	0.54	0.74	1.48
2-thiophenethiol	0.24	0.43	0.17	0.04	0.05	0.05
5-methyl-2-furfural	0.05	0.08	0.05	0.03	0.03	0.03
2-furanmethanol	0.08	0.13	0.12	0.09	0.08	0.06
2-acetylpyrrole	0.04	0.15	0.19	0.19	0.30	0.33
4-hydroxy-6-methyl-2-pyranone	0.02	0.08	0.07	0.02	0.03	0.03
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	b	b	b	0.03	0.06	0.09
2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one	1.33	3.57	2.86	0.52	0.58	0.59
5-imino-2-methylcyclopentan-1-ol[c]	0.18	0.55	0.45	0.07	b	b

[a] GC peak area of compound divided by GC peak area of internal standard. [b] Not detected. [c] Tentative identification.

intensity with irradiation time becomes less significant. The maximum browning intensity achieved is dependent only on the moisture content. As the moisture content increases, the maximum level of browning decreases. This further suggests that the decline in browning after 14% moisture content (Figure 1) is due to a dilution in the model system rather than to a lack of irradiation time.

Table I shows the total amount of volatiles generated from the model system at various moisture contents after 2.5 min of microwave irradiation. The total amount of volatiles increased with moisture content to a maximum at 11% moisture. At moisture contents above 11%, the amount of volatiles started to decrease. This moisture content is lower than that at which maximum browning occurred (14%). The decrease in volatiles may be associated with the lower degree of browning observed earlier or with loss through volatilization.

The heterocyclic compounds identified in this system at different moisture contents are shown in Table II. Major compounds formed are 2-thiophenethiol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, and 2-acetylfuran, which constitute 1.4, 32.2, and 3.9% of the total volatiles at 11% moisture, respectively. A majority of the compounds were produced in maximum amounts at 11% moisture. However, the amounts of 2-acetylfuran and 2-acetylpyrrole increased with moisture content. 2-Methylpyridine did not show significant changes with changes in moisture content.

Furans are one class of heterocyclic compounds that have been reported in a wide variety of food systems (Maga, 1979). Compounds such as 2-furfural, 2-acetylfurfural, and 5-methylfurfural are known to be thermal degradation products of glucose (Heyns et al., 1966) and have been identified in heated glucose (Shaw et al., 1970). The formation of these furan derivatives suggests that during microwave irradiation at low moisture content dehydration is the major mechanism involved. It also suggests that microwave irradiation results in a low degree of sugar fragmentation (Shibamoto and Bernhard, 1977).

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Registry No. L-Cysteine, 52-90-4; D-glucose, 50-99-7; water, 7732-18-5; 2-methylpyridine, 109-06-8; thiazole, 288-47-1; 2-furaldehyde, 98-01-1; 2-acetylfuran, 1192-62-7; 2-thiophenethiol, 7774-74-5; 5-methyl-2-furfural, 620-02-0; 2-furanmethanol, 98-00-0; 2-acetylpyrrole, 1072-83-9; 4-hydroxy-6-methyl-2-pyranone, 675-10-5; 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 3658-77-3; 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, 28564-83-2; 5-imino-2-methylcyclopentan-1-ol, 136044-25-2.