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Role of Glucose in the Maillard Browning of Maltose and Glycine: A Radiochemical Approach

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We followed the contribution of released glucose to the formation of melanoidins in the maltose−glycine reaction by adding ^{14}C glucose to the maltose−glycine mixture, after it already had undergone some reaction. This approach allowed us to confirm the turnover of glucose in this reaction and hence the role of glucose in forming melanoidins. A comparison of the total amount of glucose converted into the melanoidins with the total concentration of melanoidins formed from maltose and glycine showed that the concentration of melanoidins originating from the released glucose was relatively small in comparison to the total melanoidins concentration. Hence, the parallel glucose−glycine reaction is considered to be only a minor pathway in the formation of maltose−glycine melanoidins. The incorporation of glucose into the nondialyzable melanoidins in the maltose−glycine reaction was in excellent agreement with the amount estimated from a kinetic model for the reaction of maltose with glycine. The rate constants were estimated by nonlinear regression, via multiresponse modeling.

KEYWORDS: Maillard reaction; nonenzymatic browning; kinetic model; maltose; glucose; glycine; melanoidins

INTRODUCTION

Whereas much attention has been given to the mechanism and kinetics of the browning of sugars such as glucose and fructose and other monosacccharides, food components important with regard to browning and flavor formation include disaccharides such as lactose in milk and maltose (plus higher oligomers of glucose) when hydrolysis of starch has taken place. Little is still known about their mechanism of browning

In the initial stage of the Maillard reaction, disaccharides (as aldehydes in the open-chain form) form a Schiff base with amino groups of amino acids and are subsequently transformed via the Amadori rearrangement into the Amadori rearrangement product in the same manner as described previously for monosaccharides (*1*). As in the Maillard reaction of monosaccharides, there are two general pathways, namely, the 3-deoxyosulose-pathway via 1,2-enolization, chiefly at pH < 5, and the 1-deoxyosulose-pathway via 2,3-enolization, chiefly at neutral and alkaline pH (*2*−*4*). However, a third route, the 4-deoxyosulose-pathway, is significant for disaccharides under slightly alkaline conditions (*5*). Nevertheless, each route leads to deoxyglucosuloses (DG) which undergo enolization, cyclization, and elimination of water (*6*).

The 3-deoxyglucosulose (3-DG)-pathway leads to known advanced Maillard reaction products such as hydroxymethylfurfural (HMF) and pyrraline. Pyralline formation is favored by higher concentrations of primary amines and can be detected in heated food, where it can be formed from mono- and disaccharides (*5*, *7*). It was found that, at pH 5, 1-DG-derived compounds can also be formed, mainly glycosylisomaltol and acetylpyrrole (*5*). In the 1-DG-pathway, disaccharides differ from monosaccharides because of the 1,4-glycosidic linkage. The glycoside-linked sugar in maltose or lactose causes a degradation pathway which gives rise to typical disaccharide products. Cyclization and enolization of the 1-DG lead to five- or six-membered rings (β-pyranone and 3-furanone, respectively). Thus, evidence shows that the Maillard reaction of 1,4-linked disaccharides leads to the formation of products that on one hand are known to arise from monosaccharides and, on the other hand, are characteristic of the disaccharide from which they were obtained.

Little is known about the advanced products derived from 4-DG. Pischetsrieder and Severin (*5*) were able to isolate and identify two aminoreductones (4-deoxyaminoreductone and 5,6-dihydro-3-hydroxypyridine) which were obviously formed from this intermediate. It was assumed that they are derived only from 1,4-linked disaccharides, since the formation of the intermediate 4-DG from this type of sugar is favored. The substances referred to above also represent intermediates that can undergo further reactions, particularly with proteins and amino acids, possibly to form cross-links (*8*).

Investigations into the generation of α-dicarbonyl compounds from mono- and disaccharides under caramelization and Maillard reaction conditions in anhydrous systems (*9*) led to a new

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proposal for the mechanism of the fragmentation of disaccharides. These authors concluded that the dicarbonyl compound is not formed directly from the parent disaccharide and postulated a mechanism in which the disaccharide is degraded by a "peeling-off" process. It was also found (*10*) that, in contrast to monosaccharides, oligosaccharides generate 1,4-dideoxyhexosulose (1,4-DDH) as the predominant α-dicarbonyl compound and proposed that the pathway leading to 1,4-DDH is favored by the glycosidic substituent at C_4.

Hofmann (*11*) suggested that the 1,4-glycosidic linkage is responsible for the lower yield of brown chromophores from disaccharides in comparison to monosaccharides. It was found that, because glucose acts as a "protecting group" of the OH function on C_4, the liberation of the color precursors normally obtained from hexoses is inhibited, thus preventing the formation of a chromophore from disaccharides.

Here, we will apply our understanding of the kinetics of browning of glucose (*12*) and the compositions of melanoidins derived from maltose (*13*) to new data concerning the kinetics of the reactions of glucose within the maltose−glycine reaction to demonstrate the involvement of glucose and maltose residues in the building of melanoidins.

MATERIALS AND METHODS

Chemicals. All chemical were of AnalaR grade and were supplied by Sigma Chemical Company Ltd or Aldrich Company Ltd. D-[U-^{14}C] glucose was supplied by Amersham Life Science Ltd., U.K. Emulsifier Scintillator Plus for scintillation counting was supplied by Packard Instruments, U.K. Dialysis cassettes (MW > 3500 daltons) were obtained from Pierce & Warriner, U.K. The D-maltose/D-glucose analysis kits were supplied by R-Biopharm Ltd., U.K.

Preparation of Reaction Mixtures. The reaction mixtures contained equimolar (0.25 M) concentrations of maltose and glycine in 0.2 M sodium acetate/glacial acid pH 5.5 buffer. The flasks were closed and heated in a water bath at 70.0 ± 0.1 °C. To determine their extents of browning, samples were withdrawn at timed intervals, and absorbance was measured at 470 nm against a blank containing distilled water.

Quantification of Maltose and Glucose. The measurements of D-maltose and D-glucose were carried out using an enzyme assay kit containing α-glucosidase, hexokinase, and glucose-6-phosphate dehydrogenase. To follow the concentrations of maltose and glucose during the reaction, aliquots (1 mL) of the reaction mixture were removed at timed intervals and were allowed to cool to room temperature. After appropriate dilution, the sequence of events in the enzyme assay was followed as described by the kit supplier.

Quantification of 3-Deoxyhexosulose (3-DH). *Preparation of the External Standard.* 3-Deoxyhexosulose was prepared following the method reported by Madson and Feather (*14*). The purities of the bis-(benzoylhydrazone) of 3-DH and 3-DH were checked by elemental analysis for carbon, hydrogen, and nitrogen and were in agreement with the data published by Madson and Feather (*14*) and with the theoretical compositions. The external standard for chromatography, 2-(2,3,4-trihydroxybutyl) quinoxaline, was prepared by derivatizing 3-DH with orthophenylenediamine (oPD), following the method described by Hofmann et al. (*15*, *28*).

Analysis of 3-DH in the Reaction Mixtures. At timed intervals, aliquots (5 mL) were removed from reaction mixtures and were cooled in ice water to stop the reaction. An excess of oPD (2 mmol) was added, and the mixtures were held for 3 h at 30 °C in a water bath, following the method described by Hofmann et al. (*15*, *28*). Aliquots (500 mL) of these mixtures were withdrawn and diluted with an equal volume of water. Aliquots (20 mL) of each solution were analyzed by HPLC (Waters 600E with a Rheodyne injector (20-μL loop) with a diode-array detector (Waters 996), 220−500 nm, and a stainless-steel RP-18 column (ODS-Hypersil, 250 × 4.6 mm, 5 μm) supplied by Hichrom Ltd., U.K.). A linear solvent gradient (1 mL/min) starting with a mixture (10:90, v/v) of acetonitrile and ammonium formate buffer (pH: 3.5; 20 mM) increased acetonitrile content to 30% over 50 min. Quantification of the derivatives (at 320 nm) was carried out using the synthetic compound as external standard.

Quantification of Melanoidins. To measure the concentration of melanoidins, absorbance−time data were obtained as described above. As shown by Wedzicha and Leong (*12*), the extinction coefficient of melanoidins can be calculated from their absorbances and the amounts of sugar incorporated into their structures. The latter can be measured radiochemically. The extinction coefficient of melanoidins from the maltose−glycine reaction is 651 mol^{-1} L cm^{-1} (*13*). The extinction coefficient obtained in this way does not necessarily represent the extinction coefficient of the products in the reaction mixture as a whole, since the values were derived using dialyzed samples containing only high molecular weight melanoidins with a molecular weight cut off >3500 Daltons. Nevertheless, for the glucose−glycine reaction, Wedzicha and Leong (*12*) found that the value obtained in this way was representative of the products (low and high MW) in the reaction mixtures as a whole. It is assumed here that this conclusion applies also to maltose−glycine reaction.

Incorporation of Glucose into the Maltose−Glycine Melanoidins. A reaction mixture containing maltose and glycine (0.25 M) and acetate buffer (0.2 M) was prepared and heated at 70 ± 0.1 °C. After 86 h of heating, the reaction was spiked with 1.85 MBq D-[U-^{14}C] glucose. Aliquots (2 mL) of each reaction mixture were withdrawn at timed intervals, injected into dialyses cassettes (MW > 3500 Daltons), and dialyzed continuously against water for 10 days. After dialysis, the contents of the cassettes (retentates) were transferred into 10-mL volumetric flasks and were made up to the mark with water. Aliquots of these diluted retentates (1 mL) were mixed with 10 mL scintillation fluid and counted (Tri-carb 1900TR, Packard Instruments, U.K.) for 100 min.

At that time of addition of labeled glucose, the concentration of glucose in the maltose−glycine reaction mixture was 7.9 mM. Therefore, the ^{14}C-specific activity of glucose at $t = 86$ h was calculated by taking the initial ^{14}C-activity of 1 mL of the reaction mixture (41 119 ± 457 cpm) minus the background counts (25 ± 2 cpm), multiplying this by the dilution factor (100), and dividing by the number of moles of glucose at each time as follows:

$$\frac{(41\,119 \pm 457 - 25 \pm 2) \times 100}{7.9 \times 10^{-6}} = 5.19 \pm 0.06 \times 10^{11}\left[\frac{\text{cpm}}{\text{mol}}\right]$$

RESULTS AND DISCUSSION

Kinetic Model of the Maltose−Glycine Reaction. At Leeds, analytical solutions for the integration of the rate equations to determine the rate constants for a wide range of sugar−amino acid reaction mixtures have been used successfully (*12*, *16*−*18*). To identify the role of known intermediates in the kinetics of the Maillard reaction, it is attempted here to develop a kinetic model that takes account of the possible differences in the browning reactions of monosaccharides and disaccharides. The mechanisms of the disaccharide−glycine browning reactions are likely to be more complicated than those of the monosaccharide. A possible kinetic model for the reaction of maltose or lactose with casein at neutral pH and 120 °C was established by Brands et al. (*19*) using multiresponse modeling. By comparing the kinetic model for the disaccharides compared to that for monosaccharide (*20*), it was concluded that some degradation products are hindered by the glycosidic linked sugar in the disaccharide reaction but other routes are favored, an observation also made by Pieschetsrieder and Severin (*5*).

The kinetic model proposed here for the maltose−glycine reaction is based on the best available understanding of the key steps in the browning of maltose as illustrated in **Figure 1**, whereby we consider two distinct routes by which maltose can

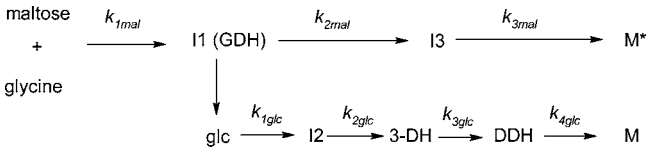

Figure 1. Proposed kinetic model for the browning of maltose–glycine mixtures. k_{1mal}, k_{2mal}, k_{1glu}, k_{2glu}, k_{3glu}, and k_{3mal} are the rate constants; I1(GDH) = intermediate 1 (it is suggested to be 4-glucosyl-3-deoxyhexosulose); I2 and I3 = intermediate 2 and 3; glc = glucose, 3-DH=3-deoxyhexosulose, DDH = 3,4-dideoxyhexosulose, M and M* = melanoidins formed from either glucose or maltose (*).

form melanonidins with glycine as already reported (*13*) in an investigation into the composition of melanoidins from glucose and maltose. First, the maltose residue can remain intact to be incorporated whole as the melanoidins increase in size. We assume that maltose reacts with glycine in the first rate-determining step, described by k_{1mal}, to form an intermediate I1, where the substituent in position 4 of the reducing sugar moiety is a glucose molecule linked by a glycosidic bond. I1 is suggested to be the 4-glucosyl-3-deoxyhexosulose (GDH). If the glycosidic bond is not broken and glucose is released, this intermediate reacts in two steps described by k_{2mal} and k_{3mal} via a further intermediate I3 toward the melanoidins. This route leads to maltose specific products (M*) which cannot be formed from the monosaccharide.

As reported in the literature (*5*, *13*), products originating from the released monosaccharide are also found in the Maillard reaction of the parent disaccharide. In the kinetic model presented here, we believe that the glycosidic bond of maltose can be broken and that glucose is released by a mechanism where the 4-substituted intermediate I1 is converted to I3, which in the specific case of maltose is 3,4-dideoxyhexosulos-3-ene DDH, by analogy to the loss of a water molecule as 3-DH is converted to DDH in the glucose−glycine reaction. As a consequence, both maltose and glucose would form DDH, a known precursor of melanoidins (*21*). The parallel reaction of the so-formed glucose to 3-DH via I2 is described by k_{1glu} and k_{2glu}, followed by the conversion of 3-DH to DDH, described by k_{3glu}. DDH is converted into melanoidins (k_{4glu}) in a single step (*12*). The reaction of glucose with glycine to form melanoidins has been studied separately by us (*22*) and requires four rate-determining steps to describe the kinetics properly and not, as reported earlier, three rate-determining steps (*12*, *15*, *16*). The three-step kinetic model was shown to account for (a) the formation of DH (3-deoxyhexosulose), (b) the conversion of DH to some activated complex (I), possibly DDH (*15*), and (c) the conversion of "I" melanoidins. In the present investigation, the formation of 3-DH was measured for the first time during our kinetic runs, and it was found that, to model the formation of it correctly, 3-DH is not formed as previously suggested in one step but it is the product of a consecutive reaction involving two rate-determining steps from glucose. Possible contenders for the first significant intermediate in the reaction could be the first Schiff base or the 1,2-enolamine. Moreover, Martins et al. (*23*) proposed a reaction network model where the glucose−glycine reaction results in an intermediate, which was suggested to be the 1,2-enaminol or the cation of the Schiff base, prior to the formation of 3-DH. It was found that, for the purposes of modeling, this intermediate had to be included as an intermediate step. This is in agreement with the findings reported here.

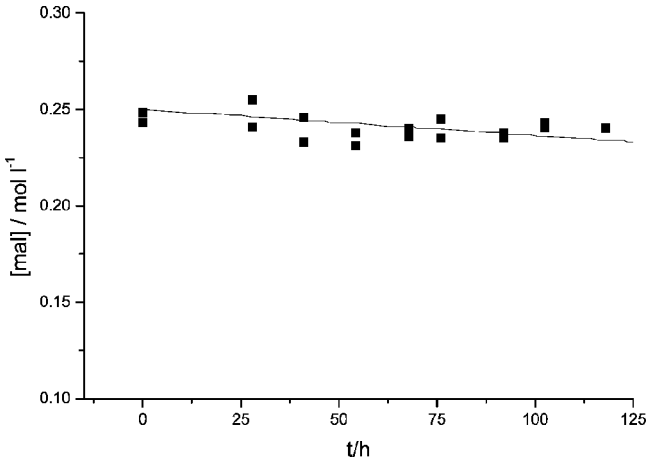

Figure 2. [Maltose], time data for the reaction of maltose (0.25 M) with glycine (0.25 M) buffered in 0.2 M sodium acetate pH 5.5; T = 70 °C. The line represents the model prediction.

The kinetic model of the browning reaction of maltose with glycine can be applied through the following set of rate equations:

$$-\frac{d[\mathrm{Mal}]}{dt} = k_{1mal}[\mathrm{Mal}] \quad (1)$$

$$\frac{d[\mathrm{I1}]}{dt} = k_{1mal}[\mathrm{Mal}] - k_{2mal}[\mathrm{I1}] \quad (2)$$

$$\frac{d[\mathrm{Glc}]}{dt} = k_{2mal}[\mathrm{I1}] - k_{1glu}[\mathrm{Glc}] \quad (3)$$

$$\frac{d[\mathrm{I2}]}{dt} = k_{1glu}[\mathrm{Glc}] - k_{2glu}[\mathrm{I2}] \quad (4)$$

$$\frac{d[3-\mathrm{DH}]}{dt} = k_{2glu}[\mathrm{I2}] - k_{3glu}[3-\mathrm{DH}] \quad (5)$$

$$\frac{d[\mathrm{DDH}]}{dt} = k_{3glu}[3-\mathrm{DH}] - k_{4glu}[\mathrm{DDH}] \quad (6)$$

$$\frac{d[I3]}{dt} = k_{2mal}[I1] - k_{3mal}[I3] \quad (7)$$

$$\frac{d[\mathrm{M}]}{dt} = \underset{M^*}{k_{3mal}[\mathrm{I3}]} + \underset{M}{k_{4glu}[DDH]} \quad (8)$$

Van Boekel (*24*, *25*) introduced multiresponse modeling to the study of Maillard reaction kinetics to allow reliable parameter estimation using complex models to fit the kinetic data. The advantage of multiresponse modeling lies in the way that information from various responses (concentrations of reactants, intermediates, and products) is combined, and a higher level of model discrimination can be achieved (*26*, *27*). The software package Athena Visual Workbench offers easy numerical integration of the rate equations and provides an environment for multiresponse modeling and parameter estimation. The measured responses in this investigation were the concentrations of maltose, glucose, 3-DH, and melanoidins.

The results of the best fits, together with the experimentally measured responses, are shown in **Figures 2**−**5**. These graphs show that the model proposed above predicts satisfactorily the loss of maltose and the formation of 3-DH and the melanoidins. The calculated formation of glucose was not as good a fit as the other responses but, nevertheless, the result is considered to be acceptable. The calculated kinetic parameters (±95% confidence limits) were as follows: $k_{1mal} = (5.55 \pm 0.13) \times 10^{-4}$ mol L^{-1} h^{-1}; $k_{2mal} = (5.91 \pm 0.40) \times 10^{-2}$ h^{-1}; $k_{1glu} =$

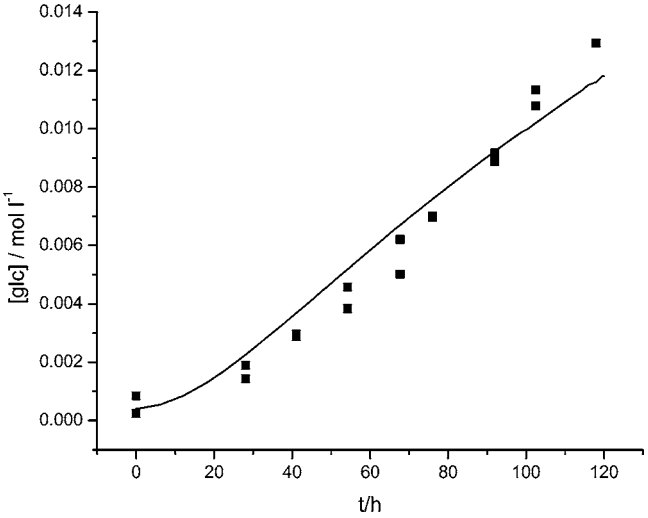

Figure 3. [Glucose], time data for the reaction of maltose (0.25 M) with glycine (0.25 M) buffered in 0.2 M sodium acetate pH 5.5; $T = 70$ °C. The line represents the model prediction.

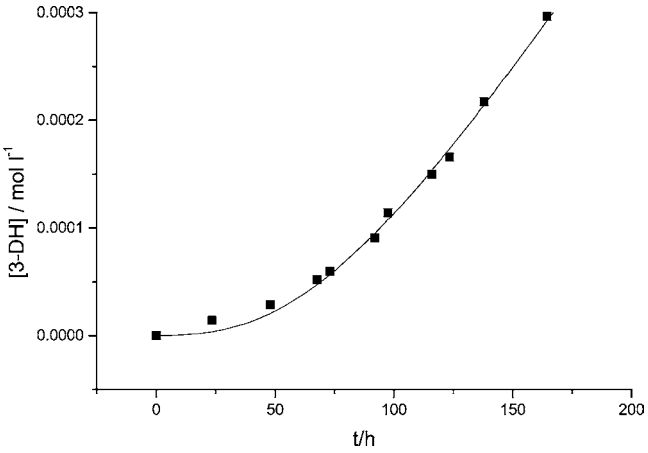

Figure 4. [3-DH], time data for the reaction of maltose (0.25 M) with glycine (0.25 M) buffered in 0.2 M sodium acetate pH 5.5; $T = 70$ °C. The line represents the model prediction.

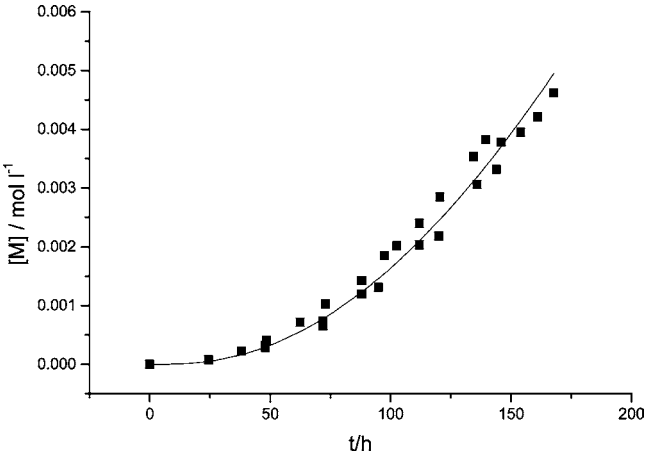

Figure 5. [Melanoidin], time data for the reaction of maltose (0.25 M) and glycine (0.25 M) buffered in 0.2 M sodium acetate pH 5.5; $T = 70$ °C. The line represents the model prediction.

$(4.33 \pm 0.21) \times 10^{-3}$ h^{-1}; $k_{2glu} = (7.68 \pm 0.45) \times 10^{-3}$ h^{-1}; $k_{3glu} = (8.75 \pm 0.29) \times 10^{-2}$ h^{-1}; $k_{3mal} = (3.65 \pm 0.12) \times 10^{-3}$ h^{-1}.

Involvement of Glucose in the Formation of Maltose−Glycine Melanoidins. To investigate the formation of glucose during the browning of maltose and its contribution to the formation of melanoidins, U-^{14}C-labeled glucose was added to the maltose−glycine reaction mixture after 86 h, at which point the concentration of the released glucose was 7.9 mM. The reason glucose was not added at the beginning of the reaction is that the aim was to label the pool of glucose, which would not exist at the start of reaction. In the kinetic model, it is assumed that glucose, after it is released, undergoes a Maillard reaction with glycine. Hence, intermediates derived directly from glucose should become incorporated into the melanoidins of the maltose−glycine reaction. This is a critical experiment insofar as it allows the turnover of glucose in this reaction to be confirmed and hence the role of glucose in forming melanoidins. The model describes the mechanism in the same way as before, but now it is intended to distinguish between the melanoidins originating from the released glucose (M) and from intermediate I3 (M*).

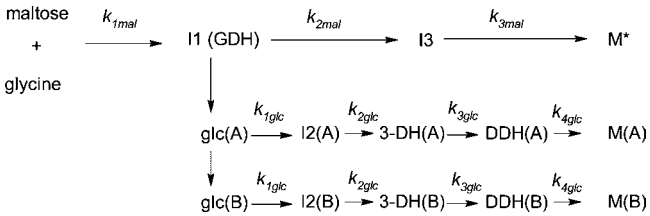

Figure 6. Kinetic model for the browning of maltose–glycine mixtures showing the formation of melanoidins formed either from maltose (M*), U-^{14}C labeled glucose (M(B)), or unlabeled glucose (M(A)), after the maltose–glycine reaction had been spiked with ^{14}C-labeled glucose. Abbreviations are used as for Figure 1.

At the moment when labeled glucose is added, all glucose present in the reaction mixture becomes labeled, and its specific activity is established by the glucose concentration and amount of ^{14}C added. As more glucose is formed, it "dilutes" the pool with inactive glucose, and some is converted to melanoidins; it is an easy matter to use the model to calculate the specific activity of the pool and of glucose molecules converted to melanoidins at any instant after introducing the label. In this way, the ^{14}C-specific activity of the melanoidins, after a given time, can be obtained, and so the contribution of the two pathways can be confirmed. An important feature of such radiolabeling studies is that the addition of the labeled glucose does not change the glucose concentration in the system significantly; the concentration of labeled glucose is negligible as is the volume of the solution added. For the purpose of calculation, the model can be written as shown in **Figure 6**. The separate pathways involving glucose are used to distinguish the participation of labeled (B) and unlabeled (A) glucose molecules. The total concentration of melanoidins is given by $[M]_{total} = [M^*] + [M(A)] + [M(B)]$, and the model values were predicted by finite increment integration of the rate equations using the values of rate constants given above. No new parameters were introduced, and no adjustments were made to existing parameters. The calculated concentrations of unlabeled glucose (A), labeled glucose (B), and total glucose, together with experimental values for total glucose, are given in **Figure 7**.

The graph shows that unlabeled glucose (glc(A)) is formed as expected. At 86 h of reaction, the discontinuity in the graph is due to the addition of the labeled glucose. The subsequent gradual fall in the concentration of ^{14}C-labeled glucose (glc-(B)) is the result of isotope dilution by unlabeled glucose as

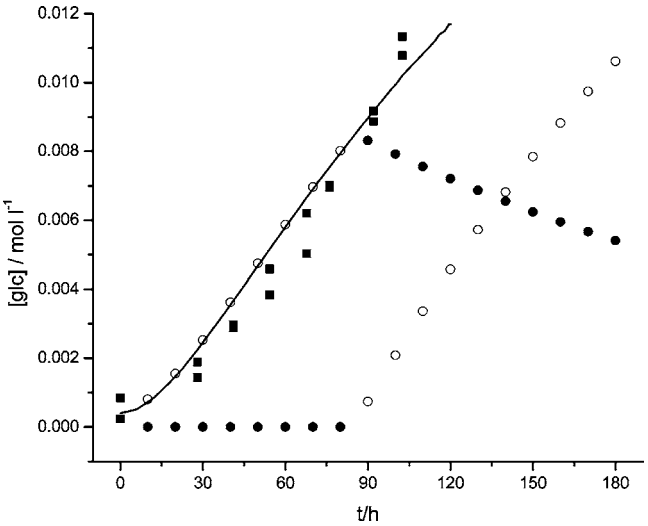

Figure 7. Formation of ^{14}C-labeled and nonlabeled glucose in the reaction of maltose (0.25 M) with glycine (0.25 M) buffered in 0.2 M sodium acetate, pH 5.5; T = 70 °C; ■, total [glc]; ——, total [glc] calculated; ●, U-^{14}C labeled [glc]; ○, unlabeled [glc].

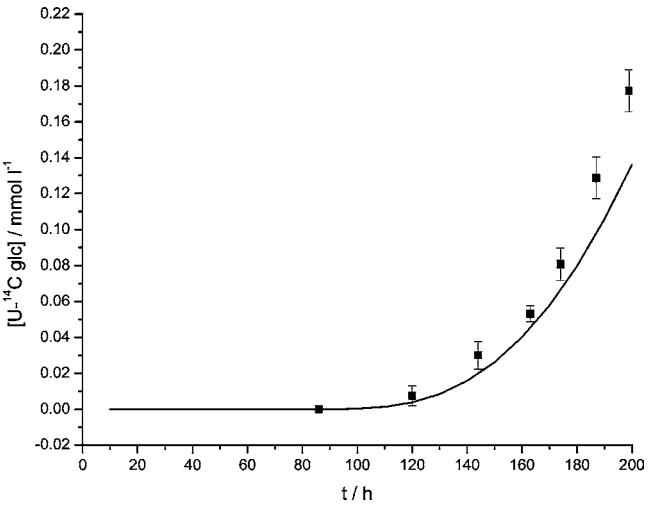

Figure 8. Calculated and experimentally determined incorporation of U-^{14}C-glucose into the melanoidins formed from the reaction of maltose (0.25 M) with glycine (0.25 M) buffered in 0.2 M sodium acetate pH 5.5; T = 70 °C; ■, M(B) found; ——, M(B) calculated.

the total concentration of glucose continues to increase and as some is converted to melanoidins.

The incorporation into melanoidins of ^{14}C-labeled glucose during the reaction of maltose with glycine is in remarkable agreement with the *calculated* conversion of labeled glucose into the melanoidins, on the basis of the kinetic model, as shown in **Figure 8**. This observation represents an independent verification of the model because these experimental data had not been used to obtain the kinetic parameters. Comparison of the total amount of glucose going into the melanoidins with the total concentration of melanoidins formed from maltose and glycine (illustrated in **Figure 9**) shows that the melanoidins from maltose include structures which have been formed from glucose, but the amount of melanoidins originating from the released glucose is relatively small in comparison to the total melanoidin concentration. Hence, the parallel glucose−glycine reaction to form glucose specific melanoidins takes place but is not the major pathway in melanoidin formation in the maltose−glycine reaction.

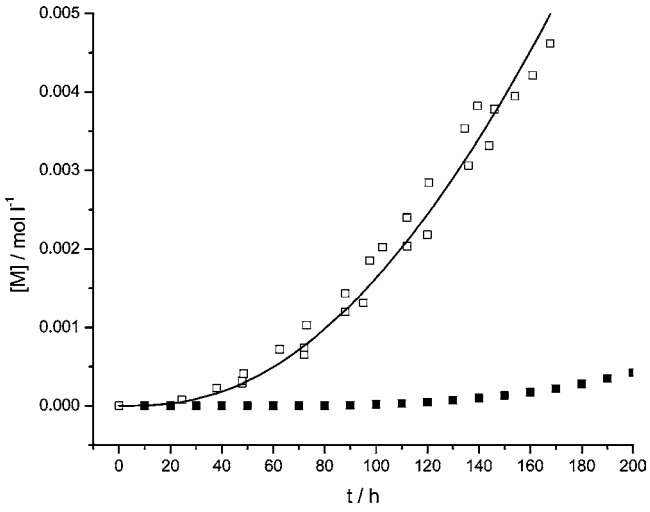

Figure 9. Calculated and experimentally determined concentrations of melanoidins (M(total)) and melanoidins formed from the released glucose (M(glc)) in the maltose–glycine reaction; [mal] = [gly] = 0.25 M buffered in 0.2 M sodium acetate, pH 5.5; T = 70 °C; □, total melanoidins concentration found; ——, total melanoidins concentration calculated; ■, total melanoidins concentration formed from glucose (M(glc) = (M(A) + M(B)).

LITERATURE CITED

(1) Kramhoeller, B.; Ledl, F.; Lerche, H.; Severin, T. HPLC separation of some characteristic components in reaction mixtures of disaccharides with amines- model system for milk and cereal products. *Z. Lebensm.-Unters.-Forsch. A* **1992**, *194*, 431−433.

(2) Ledl, F.; Schleicher, E. New aspects of the Maillard reaction in foods and in the human body. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 565−594.

(3) Nursten, H. E. Key mechanistic problems posed by the Maillard reaction. In *The Maillard reaction in Food Processing, Human Nutrition and Physiology*; Finot, P. A., Aeschebacher, H., Hurrel, R. F., Liardon, R., Eds.; 1990; pp 145−153.

(4) O'Brien, J. Heat-induced changes in lactose: isomerization, degradation, Maillard browning. In *Heat induced Changes in Milk*; Fox, P. F., Ed.; 1995; pp 134−170.

(5) Pischetsrieder, M.; Severin, T. Advanced Maillard products of disaccharides: analysis and relation to reaction conditions. In *Chemical markers for Processed and Stored Foods*; Lee, T. C., Kim, H. J., Eds.; 1996; pp 14−23.

(6) Lederer, M.; Glomb, M.; Fischer, P.; Ledl, F. Reactive Maillard intermediates leading to coloured products-5-hydroxymethyl- and 5-(1,2-dihydroxyethyl)-3(2H)-furanone. *Z. Lebensm.-Unters.-Forsch. A* **1993**, *197*, 889−892.

(7) Henle, T.; Klostermeyer, H. Bestimmung proteingebundener Maillard-Verbindungen in Milchprodukten mittels Ionenaustauschchromatographie und Photodiodenarraymessung. *Lebensmittelchemie* **1993**, *47*, 73−85.

(8) Pischetsrieder, M.; Severin, T.; Kramhoeller, B. Maillard reaction of Lactose and maltose. *J. Agric. Food Chem.* **1993**, *41*, 347−351.

(9) Hollnagel, A.; Kroh, L. W. Formation of α-dicarbonyl fragments from mono and disaccharides under caramelisation and Maillard reaction conditions. *Z. Lebensm.-Unters.-Forsch. A* **1998**, *207*, 50−54.

(10) Hollnagel, A.; Kroh, L. W. Degradation of oligosaccharides in nonenzymatic browning by formation of α-dicarbonyl compounds via a "peeling off" mechanism. *J. Agric. Food. Chem.* **2000**, *48*, 6219−6226.

(11) Hofmann, T.; Frank, O. On the influence of the carbohydrate moiety on chromophore formation during food-related Maillard

reaction of pentoses, hexoses, and disaccharides. *Helv. Chim. Acta* **2000**, *83*, 3246−3261.
(12) Wedzicha, B. L.; Leong, L. P. A critical appraisal of the kinetic model for the Maillard browning of glucose with glycine. *Food Chem.* **2000**, *68*, 21−28.
(13) Mundt, S.; Wedzicha, B. L. A comparative study of the composition of Maillard polymers fromglucose and maltose. *J. Agric. Food Chem.* **2004**, *52* (13), 4256−4260.
(14) Madson, M. A.; Feather, M. S. An improved preparation of 3-deoxy-D-erythro-hexos-2-ulose via the bis(benzoylhydrazone) and some related constitutional studies. *Carbohydr. Res.* **1981**, *94* (2), 183−191.
(15) Hofmann, T.; Bors, B.; Stettmaier, K. Studies on radical intermediates in the early stage of the nonenzymatic browning reaction of carbohydrates and amino acids. *J. Agric. Food Chem.* **1999**, *47*, 379−390.
(16) Wedzicha, B. L.; Kedward, C. Kinetics of the oligosaccharide-glycine-sulphite reaction: relationship to the browning of oligosaccharide mixtures. *Food Chem.* **1995**, *54* (4), 397−402.
(17) Davies, C. G. A.; Wedzicha, B. L.; Gillard, C. Kinetic model of the glucose-glycine reaction. *Food Chem.* **1997**, *60*, 323−329.
(18) Mundt, S.; Wedzicha, B. L. A kinetic model for the glucose-fructose-glycine browning reaction. *J. Agric. Food Chem.* **2003**, *51* (12), 3651−3655.
(19) Brands, C. M. J.; van Boekel, M. A. J. S.. Kinetic modelling of reactions in heated disaccharide-casein systems. *Food Chem.* **2003**, *83*, 13−26.
(20) Brands, C. M. J.; van Boekel, M. A. J. S. Kinetic modelling of reactions in heated monosaccharide-casein systems. *J. Agric. Food Chem.* **2002**, *49*, 4667−4675.
(21) Reynolds, T. M. Chemistry of non-enzymic browning I. The reaction between aldoses and amines. *Adv. Food Res.* **1963**, *12*, 1−52.
(22) Mundt, S. The kinetics of disaccharide browning: maltose and lactose. PhD dissertation, University of Leeds, United Kingdom, 2002.
(23) Martins, S. I. F. S.; van Boekel, M. A. J. S. A kinetic model for the glucose/glycine reaction pathways. *Food Chem.* **2005**, *90*, 257−269.
(24) Van Boekel, M. A. J. S. Statistical aspects of kinetic modelling for food science problems. *J. Food Sci.* **1996**, *61* (3), 477−485.
(25) Van Boekel, M. A. J. S. Effect of heating on Maillard reactions in milk. *Food Chem.* **1998**, *62*, 403−414.
(26) Stewart, W. E.; Caracotsios, M.; Sørensen, J. P. Parameter estimation from multiresponse data. *AIChE J.* **1992**, *38* (5), 641−650.
(27) Box, M, J.; Draper, N. R. The Bayesian estimation of common parameters from several responses. *Biometrika* **1965**, *52*, 355−365.
(28) Hofmann, T. Quantitative studies on the role of browning precursors in the Maillard reaction of pentoses and hexoses with L-alanine. *Carbohydr. Res.* **1998**, *313*, 215−224.

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