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Effects of pH on Caramelization and Maillard Reaction Kinetics in Fructose-Lysine Model Systems

E.H. AJANDOUZ, L.S. TCHIAKPE, F. DALLE ORE, A. BENAJIBA, AND A. PUIGSERVER

ABSTRACT: The nonenzymatic browning reactions of fructose and fructose-lysine aqueous model systems were investigated at 100 °C between pH 4.0 and pH 12.0 by measuring the loss of reactants and monitoring the pattern of UV-absorbance and brown color development. At all the pH values tested, the loss of fructose was lower in the presence than in the absence of lysine. And, in lysine-containing fructose solution, the sugar disappeared more rapidly than the amino acid. Lysine was moderately lost below pH 8.0. Caramelization of fructose, which accounted for more than 40% of total UV-absorbance and 10 to 36% of brown color development, may therefore lead to overestimating the Maillard reaction in foods.

Keywords: Maillard reaction, caramelization, lysine, fructose

Introduction

THE MAILLARD REACTION, WHICH links the carbonyl group of reducing carbohydrates and the amino group of free amino acids as well as of lysyl residues in proteins, may have either beneficial or detrimental effects. At early stages of the reaction, an improvement of the functional properties of proteins was generally observed (Handa and Kuroda 1999), and afterwards antioxidant compounds are formed (Monti and others 1999) as well as highly appreciated browned flavors (Ho 1996). However, loss of lysine and decrease in protein digestibility may also occur (Friedman 1996), together with some antinutritive (Oste and others 1987; O'Brien and others 1994), toxic (O'Brien and Morrissey 1989) or mutagenic (Wang and others 1999) effects. The caramelization of sugars, which takes place at the same time, also contributes to nonenzymatic browning reactions. In both the Maillard and caramelization reactions, highly UV-absorbing and colorless compounds are formed at intermediate stages, whereas the brown polymers are formed at final stages (Hodge 1953; Mauron 1981).

The nonenzymatic browning reaction of fructose has not been as thoroughly investigated as that of glucose, and it has usually been compared to the latter. In several early studies (Maillard 1912; Hodge 1953; Reynolds 1965), the browning of fructose aqueous solutions in the presence of amino acids in model systems was found to take place more rapidly than that of glucose, although the contrary was also reported to occur (Ellingson and others 1954; Bobbio and others 1981; Baxter 1995). It has also been reported that the browning of fructose solutions was either more or less extensive than that of glucose, depending on the heating conditions (Kato and others 1969; Buera and others 1987; Wijewickreme and others 1997). On the other hand, the influence of pH on the Maillard reaction of amino acid-containing glucose or fructose model systems has been studied at different pH ranges and conditions of temperature and concentration of reactants, namely pH 4-6 (Buera and others 1987), pH 5-7 (Petriella and others 1985), pH 5.5-7.5 (Baxter 1995) and pH 6-12 (Ashoor and Zent 1984). It is worth mentioning here that only the Maillard browning intensity was measured in most of these studies.

Very little attention has been paid so far to the contribution of caramelization to the nonenzymatic browning reactions of glucose or fructose, although studying the chemical reactions involved in caramelization is a prerequisite for understanding the Maillard reaction (Mauron 1981). It has, however, been clearly established that the fragmentation of sugars occurs to a significant extent at pH values below neutrality (O'Beirne 1986; Buera and others 1987) and increases considerably at high pH values and temperatures, yielding colored N-free polymers (Myers and Howell 1992; Clarke and others 1997). The Maillard reaction in foods may then be overestimated and the emphasis placed on its detrimental rather than its beneficial effects.

The aim of this study was, therefore, to describe the kinetics of the nonenzymatic browning reaction in fructose solutions heated either alone or in the presence of lysine at 100 °C at initial pH values ranging from 4.0 to 12.0. The extent of both the caramelization and the Maillard reactions was compared at the initial, intermediate, and final stages. The kinetic behavior of the nonenzymatic browning reactions of fructose was also compared to that of glucose under the same experimental conditions (Ajandouz and Puigserver 1999).

Materials and Methods

Materials

L-lysine, D-fructose, L-α-amino-n-butyric acid and triethylamine (TEA) were purchased from Sigma Chemical Co. (St. Louis, Mo., U.S.A.). Phenylisothiocyanate (PITC) and the standard mixture of amino acids were supplied by Pierce Chemical Co. (St. Louis, Mo., U.S.A.). All the other chemicals used were of the purest commercially available grade.

Heating procedure

An equimolar (0.05 M) mixture of fructose and lysine (3 mL) was heated in a 15-ml screw-sealed tubes for various periods of time in boiling water at various pH values. After 5, 15, 30, 60, 90, and 120 min, the tubes were removed and immediately cooled in ice. Part of the heated solution was used directly for UV-absorbance, browning, and final pH measurements, while the rest was

stored at –20 °C for fructose and lysine loss determinations. Fructose and lysine were separately heated under the same experimental conditions. The following buffers were used: 0.05 M sodium acetate adjusted to pH 4.0 with 1 M acetic acid, 0.05 M sodium phosphate adjusted to pH 6.0, pH 7.0 and pH 8.0 using either monobasic or dibasic sodium phosphate, 0.05 M Tris-carbonate adjusted to pH 9.0 with 1 M hydrochloric acid, 0.05 M sodium carbonate-bicarbonate adjusted to pH 10.0 and pH 11.0 using either sodium carbonate or sodium bicarbonate, and finally 0.05 M sodium bicarbonate adjusted to pH 12.0 with 1 M sodium hydroxide.

Fructose loss

The remaining nondegraded fructose was monitored on high-performance anion exchange-pulsed amperometric detection equipment. Fructose was eluted under isocratic conditions from the CarboPac PA-100 (Dionex Corp., Sunnyvale, Calif., U.S.A.) analytical anion exchange column (250 × 4 mm) equipped with an IonPac AG4A-SC (Dionex Corp., Sunnyvale, Calif., U.S.A.) guard column (25 × 4 mm) connected to a gold working electrode cell. The eluent, a 5 mM sodium acetate solution containing 0.1 M NaOH, was delivered at a rate of 1 mL.min^{-1} by a GP 40 Dionex gradient pump (Dionex Corp.,). The injection volume was delivered by an AS 3500 Spectra System autosampler from Thermo Separation Products (Fremont, Calif., U.S.A.) and the detection was carried out with an ED 40 electrochemical detector (Dionex Corp.). The area under the eluted peak was integrated with an Olivetti Pentium P 75i integrator (Olivetti, Paris, France) using the Borwin chromatography Software program (JMBS, Grenoble, France), based on a 0- to 250-pmol fructose calibration chart.

Amino acid loss

The unreacted lysine was monitored by performing reverse phase high-performance liquid chromatography after pre-column derivatization with phenylisothiocyanate as described by Bidlingmeyer and others (1984). The eluted amino acid was detected at 254 nm using a model 486 variable wavelength detector (Waters Assoc., Milford, Mass., U.S.A.), and the resulting peak was integrated as described above for fructose.

UV-absorbance and brown color measurements

The UV-absorbance and browning intensity of the aqueous solutions containing fructose or fructose and lysine were measured at room temperature at 294 nm and 420 nm, respectively, using a Beckman model DU 640 spectrophotometer (Beckman Instruments, Irwin, Calif., U.S.A.). When necessary, appropriate dilutions were made in order to obtain an optical density of less than 1.5.

All the experiments were carried out in triplicate and the mean values (overall less than 10% standard deviation) were used to draw up the kinetic plots.

Results and Discussion

Early stages in the browning reactions

The initial stages in the nonenzymatic browning reaction of the heated fructose solutions, with or without lysine, was studied by measuring the extent of fructose and lysine degradation over time. As expected, an increase in pH of the heated solutions led to an increase in the initial rate of degradation of both fructose and lysine (Figure 1). Lysine degradation was already reduced at pH 8.0, since it did not exceed 22% of the amino acid after 2 h of boiling, and only 5% after 15 min as compared to higher pH values (13 to 34% loss after 15 min of heating at pH 9.0 to 12.0). Moreover, lysine loss resulted almost completely, if not exclusively, from Maillard reaction, as no significant loss was observed when the amino acid was heated in the absence of fructose. Most of the loss was, therefore, observed during the beginning of heating; a no-loss period occurred at later heating stages. A no-loss period has also been observed in a glycine-containing glucose solution stored at 37 °C (Baisier and Labuza 1992), as well as in glucose solutions containing either lysine, or methionine or threonine when heated to 100 °C at different pH values (Ajandouz and Puigserver 1999). In a number of studies in which proteins were heated in the presence of reducing sugars at an intermediate moisture content and a wide range of temperatures, a no-loss period was found to occur when 50 to 75% of the lysine was destroyed (Wolf and Thompson 1977; Labuza and Saltmarch 1981). The no-loss period might be due to some limitation in the reactants or to the release of amino groups at advanced stages of the Maillard reaction. The decrease in pH throughout the heat treatment may also contribute to the progressive lowering of the rates of lysine loss. Under our experimental conditions, a pH drop of 0.25-3.8 units and of 0.5 to 1.8 units occurred in fructose and fructose-lysine model systems after a 2-h heating period at starting pH values of 6.0 to 12.0, respectively. A more severe pH decrease has been reported in unbuffered solutions of glycine and glucose (Nicoli and others 1993). More attention should, therefore, be paid to the pH decrease during nonenzymatic browning reactions, especially at intermediate moisture content and pH values below neutrality.

Studies on the Maillard reaction placing emphasis on the degradation of reducing sugars are not so numerous. Warmbier and others (1976) have reported that lysine loss was higher than that of glucose in a casein-glucose-glycerol model system at 45 °C and a a_w value ranging from 0.57 to 0.85, whereas Baisier and Labuza (1992) have shown that glycine and glucose losses occurred with the same rate constant in a solution stored at 37 °C. More recently,

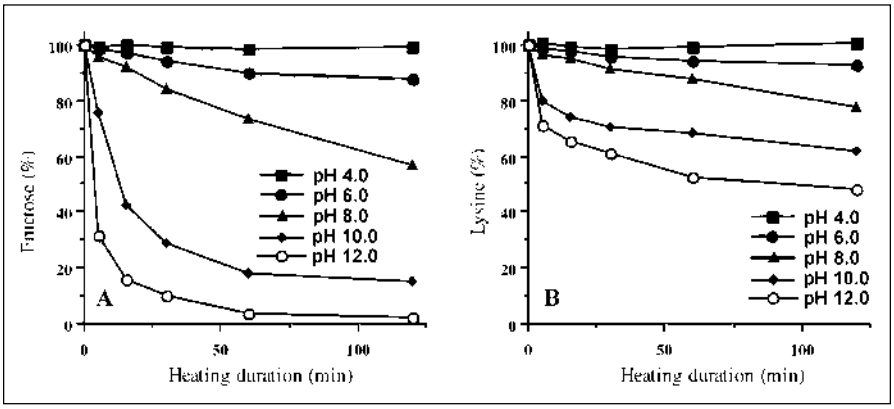

Figure 1—Time course of fructose (A) and lysine (B) loss in lysine-containing fructose solutions when heated at 100 °C and at varying pH values.

glucose was found to be more rapidly degraded than lysine, or methionine or threonine in solutions heated to 100 °C at pH values ranging from 4.0 to 12.0 (Ajandouz and Puigserver 1999). When cocoa bean extracts were heated to 150 °C for 8 min, both fructose and glucose were totally destroyed, whereas the loss of free amino acids did not exceed 50% (Mohr and others 1971). A high temperature may promote some caramelization reaction resulting in a higher degradation of reducing sugar as compared to amino acids and, consequently, in changing the amino group-to-reducing sugar molar ratio.

As shown in Figure 2, fructose degradation was actually lowered in the presence of lysine as compared to that of fructose alone. This protective effect may be due to some reversible interaction which takes place between the ketose and the amino acid, since it was particularly conspicuous at pH values between 8.0-11.0 where the 2 lysine amino groups are deprotonated. A similar protective effect has also been observed when glucose was heated in the presence of lysine, methionine or threonine (Ajandouz and Puigserver 1999). Whatever the pH conditions, the active concentration of fructose in the presence of lysine is significantly different from that in the absence of lysine, although the starting concentration of the sugar was the same. It is not really easy to define precisely the respective contribution of caramelization and Maillard reaction to the overall nonenzymatic browning.

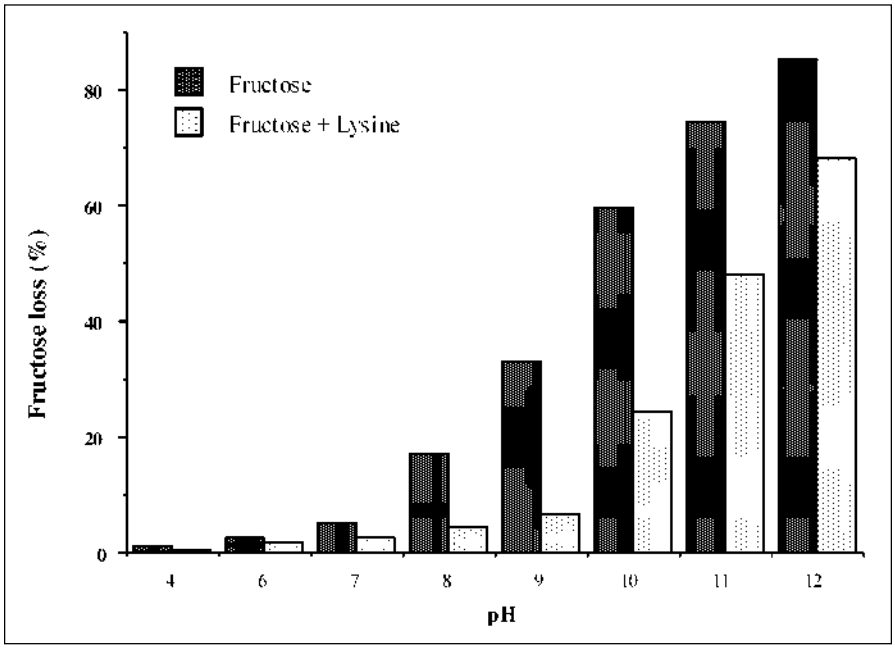

Figure 2—Percentage of fructose loss when it is heated for 5 min alone or in the presence of lysine at 100 °C and increasing pH values.

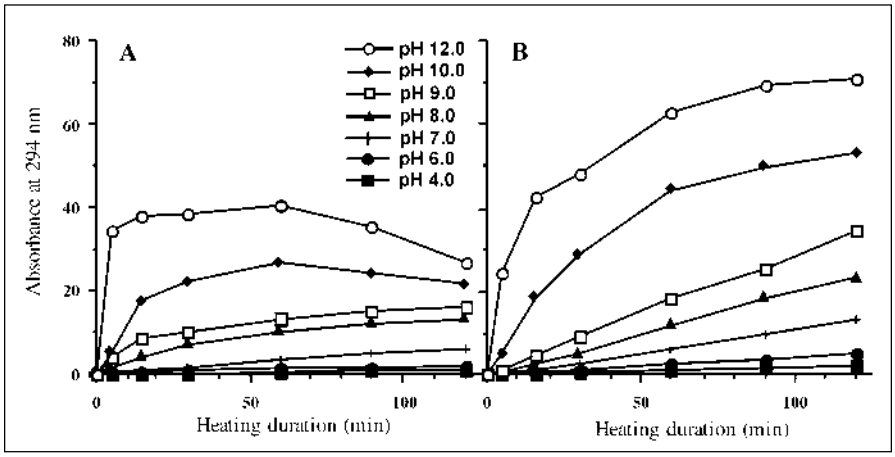

Figure 3—Time course of the appearance of UV-absorbance in aqueous solutions of fructose (A) and in lysine-containing fructose solutions (B) after heating to 100 °C at increasing pH values.

Intermediate stages

Intermediate stages in the nonenzymatic browning reactions were detected by recording the UV-absorbance at 294 nm as described by Lerici and others (1990). Figure 3 shows that, in both the absence and presence of lysine in the fructose solution, the higher the starting pH value, the higher was the absorbance. When fructose was heated alone at initial pH values ranging from 4.0 to 7.0, a progressive accumulation of the intermediate degradation products occurred as a function of time and no lag time was observed, whereas the hyperbolic curves which were obtained at pH 8.0 and pH 9.0 no doubt reflected the high level of fructose degradation occurring during the initial stages of the heating period (Figure 2). At higher pH values, the UV-absorbance quickly reached the maximum value and decreased thereafter, in agreement with the almost complete degradation of fructose during the 1st stages in the heating period. The decrease in the UV-absorbance may result from the transformation of some intermediate products into brown polymers. In the presence of lysine, the amount of intermediate products accumulated was higher than in the absence of lysine and fitted a zero-order reaction model up to pH 9.0, as compared to pH 7.0 in the absence of the amino acid. Moreover, even at pH 12.0, no decrease in the absorbance was observed. The difference found in the kinetic behavior of fructose alone, and fructose in the presence of lysine, might be due to the contribution of some Maillard reaction products to the UV-absorbance, as well as to the accelerating effect of the amino acid on sugar caramelization reaction. As stated by Mauron (1981), most reactions that occur in pure sugars only at very high temperatures take also place at much lower temperature once they have reacted with amino acids. Based on the slopes of the UV-absorbance curves of the solutions heated between pH 4.0 and pH 7.0, the caramelization reactions were found to account for as much as 40 to 62% of the UV-absorbing reaction products of fructose-lysine mixtures.

Final stages

The final stages in the nonenzymatic

browning reaction of fructose heated in the presence or absence of lysine were studied by measuring the absorbance at 420 nm. The time course of the development of the brown color at increasing pH values is shown in Figure 4. The similarity between most of these curves and the UV-absorbance curves suggests that a large proportion of the intermediate products are precursors of brown polymers. No decrease in the absorbance at 420 nm of the fructose solution was observed at pH 10.0 and at pH 12.0, in sharp contrast with the UV-absorbance and the maximum brown color value, which was reached at the beginning of the heating period, remained unchanged thereafter. The promoting effect of pH on browning development was in agreement with the literature data (Ashoor and Zent 1984; Petriella and others 1985; Buera and others 1987; Baxter 1995).

The rating of fructose caramelization as a percentage of the overall brown color intensity of the lysine-containing fructose solution between pH 4.0 and pH 7.0 was found to be between 10 and 36%. These values were lower than those obtained by Buera and others (1987) in an aqueous glycine-fructose model system heated to 55 °C, which were 25% and 43% at pH 4.0 and pH 6.0, respectively. It should be noted, however, that a 4-fold molar excess of fructose with regard to lysine was used in their study and that in addition the reactivity of lysine and glycine may not be the same.

In all cases, the caramelization reactions contributed less to the browning intensity than to the overall UV-absorbance. The UV-absorbance values are more or less representative of intermediate compounds in the nonenzymatic browning reactions (Hodge 1953; Lerici and others 1990), whereas the absorbance values at 420 nm may be related to the content in brown polymers, and the 294/420 nm absorbance ratio is indicative of the polymerization extent. Figure 5 illustrates the effect of pH on the transformation of intermediates into brown polymers in fructose and fructose-lysine model systems after a 1-h heating period at 100 °C. As regards the caramelization reaction of fructose, a pH increase from 4.0 to 8.0 strongly enhanced the polymerization of the carbonyl compounds generated by the thermal degradation of fructose, whereas at a higher pH value, the intermediates were almost equally transformed into brown polymers. When fructose was heated in the presence of lysine at a pH value between 4.0 and 8.0, formation of the intermediate polymerization products decreased, whereas above pH 8.0 the rate of polymerization reactions of the intermediate carbonyl compounds seem not to be dependent on both the pH and the presence of the amino acid. Figure 5 strongly suggests that changes in the mechanism of the nonenzymatic browning reaction occurred around pH 8.0. According to the general scheme of Hodge (1953), dealing with the chemistry of nonenzymatic browning reactions in model systems, the Amadori compounds are supposed to give rise preferentially to furfurals and related derivatives under acidic conditions, while reductones and highly reactive dicarbonyls are formed essentially under alkaline conditions.

As pointed out in the introduction, there are some conflicting data about the reactivity of fructose as compared to glucose as far as browning is concerned. With respect to the intermediate stages of the Maillard reaction, volatile compounds such as furans, pyrans, and pyrroles have been obtained in larger amounts from fructose than from glucose when each sugar was heated in the presence of â-alanine

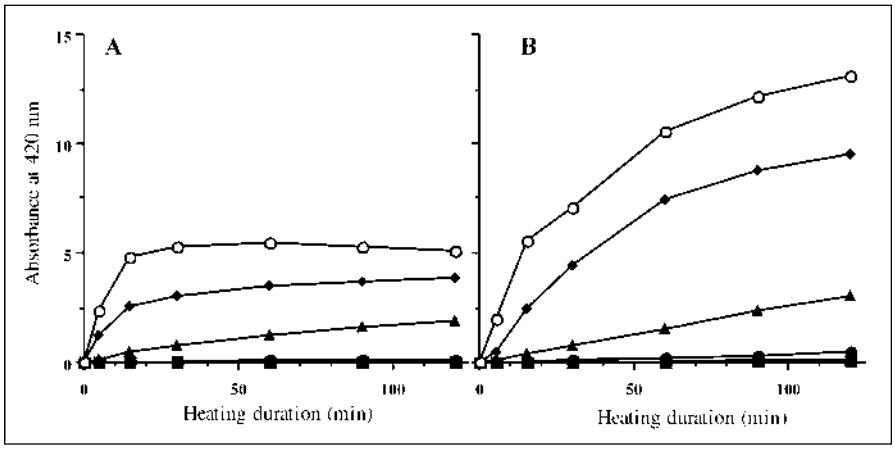

Figure 4—Time course of brown color development in aqueous solution of fructose (A) and in lysine-containing fructose solution (B) heated to 100 °C at increasing pH values. The symbols are the same as in Figure 1.

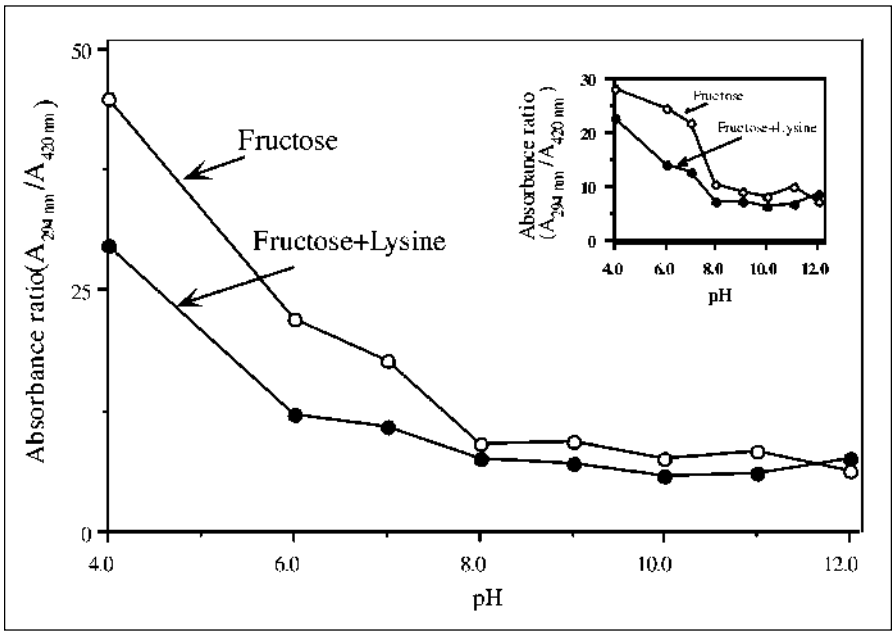

Figure 5—Influence of pH on the transformation of UV-absorbing compounds into brown polymers in fructose and lysine-containing fructose solutions heated to 100 °C for 60 min. The plots at 30 min of heating are shown in the insert.

(Nishibori and Bernhard 1993). Other products with the nitrogen atoms from amino acids, such as pyrazines (Amrani-Hemaimi and others 1995), as well as more specific products from asparagine (Shu and Lawrence 1995) were apparently formed irrespective of the nature of the reducing sugar. Some mechanistic differences seem very likely to exist between the nonenzymatic browning reaction of fructose and that of glucose as suggested, for example, by the existence of a lag time in the browning of glucose solutions and not in that of fructose solutions (Kato and others 1969; Buera and others 1987; Ajandouz and Puigserver 1999).

A possible explanation of this observation might be the formation of some rate-limiting intermediates during the nonenzymatic browning reaction of glucose, but not in that of fructose, as suggested by Kato and others (1969). In this connection, it seems very likely that multiple Heyns products rather than a single Amadori product are formed in the Maillard reaction (Suarez and others 1989). Another point which should certainly be taken into consideration when comparing the reactivity of glucose and fructose is the concomitant caramelization reactions. This should not be overlooked, as these reactions may also give rise to a variety of products from each sugar (Shaw and others 1968; Yang and Montgomery 1996). As shown in Figure 6, the caramelization reaction of glucose increased exponentially from pH 7.0 up to pH 12.0, while a linear increase in the rate of the caramelization reaction of fructose occurred in the same pH range. No further change was observed regarding the browning when lysine was added to glucose and fructose solutions.

CONCLUSION???

IN ADDITION TO YIELDING INSIGHTS into the nonenzymatic browning reaction of fructose, especially at pH values of foods (below 7.0), the results of our study may have some useful practical implications at both the food technology and nutritional levels as to how low alkaline conditions should be managed, especially regarding some plant proteins such as those from soybean which may be exposed to high alkalinity levels during their processing. Further studies are now required to be able to distinguish more clearly between the caramelization reaction and that initiated by the interaction between the sugar and protein amino groups in food. The increase in the alimentary use of free fructose during the last 2 decades, mainly in the form of high-fructose corn syrup (Park and Yetly 1993), has brought to the fore the question as to how it is degraded during heat treatment, especially at pH values above neutrality, and what reactions occur with lysine limiting proteins concomitantly with caramelization reactions. The results shown here throw some light on these questions.

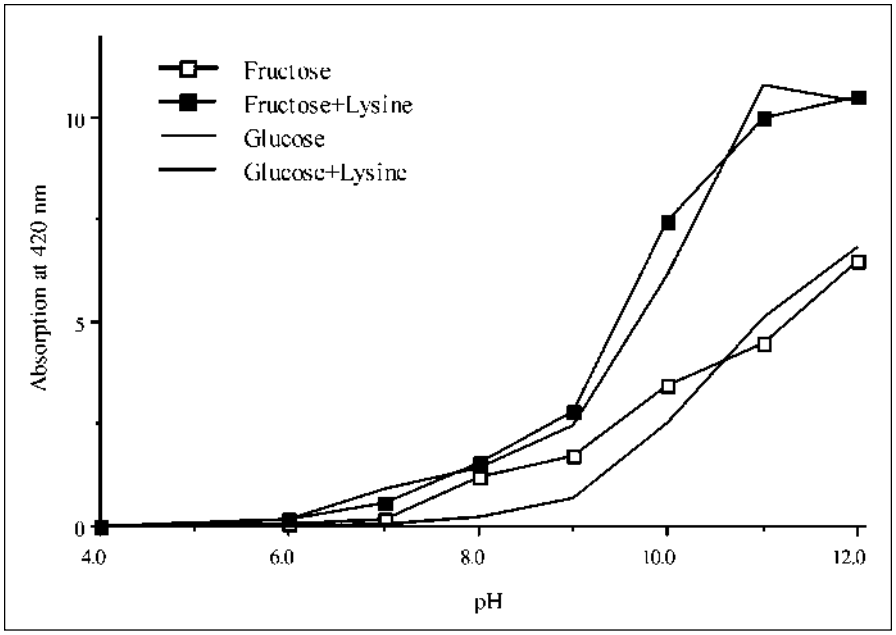

Figure 6—Effect of pH on browning development in aqueous fructose, glucose, fructose-lysine and glucose-lysine model systems heated to 100 °C for 60 min.

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