Studies with Radioactive Tracers. XVIII. Model Browning Reactions between Glycine and D-Fructose[1]

C. C. LEE and Y. H. LIAU, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

ABSTRACT

Solutions of glycine and D-fructose were applied on filter paper, air-dried, and "baked" at 120°C. for selected time intervals. The browning reactions that occurred were studied with the aid of radioactive tracers, the labeled reactants employed being glycine-1-^{14}C, glycine-2-^{14}C, or uniformly labeled D-fructose-^{14}C. 2-Deoxy-2-glycino-D-glucose (I) and 2-deoxy-2-glycino-D-mannose (II) were identified as products formed in the initial stages of the reaction, and (I) was isolated in pure crystalline form. The results also suggested that Strecker-type of decarboxylation could take place after the amino acid has combined with the reducing sugar. Changes in the radioactivity contents with lengths of time the reactants were subjected to heating were studied for the volatile, basic water-soluble, nonbasic water-soluble, and water-insoluble fractions, and the data indicate that the general trends of behavior are similar for the reactions of glycine with D-fructose and with D-glucose.

In paper XVII in this series of studies (1), model browning reactions between glycine and D-glucose, with one of the reactants labeled with ^{14}C (glycine-1-^{14}C, glycine-2-^{14}C, or uniformly labeled D-glucose-^{14}C),were investigated. The reaction conditions were chosen to simulate breadmaking by applying solutions of the reactants on filter paper and then "baking" the air-dried materials at 120°C. for the desired length of time. Besides some unreacted glycine, 1-deoxy-1-glycino-D-fructose (D-fructoseglycine), the Amadori-rearrangement product formed in the initial stages of the reaction, was obtained as the only isolable crystalline product. The variations with "baking" time in the amounts of radioactive materials in the volatile, basic water-soluble, nonbasic water-soluble, and water-insoluble fractions were also studied. The results were interpreted as in general consistent with the various processes for Maillard-type of browning reactions as originally outlined by Hodge (2). In the present work, such studies on model browning reactions were extended to include an investigation of the reactions between glycine and D-fructose.

MATERIALS AND METHODS

Studies with ^{14}C-Labeled Compounds

The methods employed were the same as described previously in paper XVII (1), except that D-fructose was used in place of D-glucose. The basic components from the reactions of glycine-1-^{14}C or glycine-2-^{14}C with D-fructose were investigated by "baking" the reactants on filter paper at 120°C. for differing lengths of time. The changes with heating time in the activities of the volatile, basic water-soluble, nonbasic water-soluble, and water-insoluble fractions were also

[1]Contribution from the Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

examined for the reactions between glycine-1-^{14}C or glycine-2-^{14}C and D-fructose, and for the heating of the basic interaction products (chiefly components A and B, as described later) derived from glycine and uniformly labeled D-fructose-^{14}C.

Isolation of Components A and B

Components A and B, formed in the initial stages of reaction between glycine-1-^{14}C or glycine-2-^{14}C and D-fructose, were isolated from a large-scale experiment with inactive materials in a manner analogous to the isolation of 1-deoxy-1-glycino-D-fructose from the reaction of glycine with D-glucose (1). Starting with 15 g. of glycine and 75 g. of D-fructose, the basic materials were eluted from a column of Dowex-50 resin (H^+ form) by 0.2N trichloroacetic acid (TCA), and then continuously extracted with ether to remove the TCA and concentrated to give about 20 g. of a yellowish syrup (1). This syrup was dissolved in 250 ml. of water and decolorized three times with activated charcoal. The resulting solution was allowed to concentrate by evaporation at room temperature, and during this evaporation some crystals were formed. This wet crystalline material (about 6 g.) was collected with a spatula, redissolved in 20 ml. of water, heated to about 60°C., and 10 ml. of hot methanol added. After the material had been cooled in a refrigerator overnight, 1.6 g. of crystals were obtained, m.p. 142° to 144°C. (decomp). To the mother liquor from this crystallization, 10 ml. of methanol was added and, on cooling in a refrigerator for 2 days, another batch of crystals weighing 2.2 g. and melting at 187° to 189°C. (charred) was collected. Each of these two batches of crystals gave a spot corresponding to component A on paper chromatography (1). These crystalline materials were, therefore, designated as A-1 and A-2, respectively. Eventually, A-1 proved to be an impure sample of the monohydrate of 2-deoxy-2-glycino-D-glucose; and A-2, pure 2-deoxy-2-glycino-D-glucose.

The residual syrup after the separation of the 6 g. of wet crystals described above, and the mother liquor from the crystallization of A-2, were combined and concentrated to give about 5 g. of syrupy material. Paper-chromatographic analysis showed that it still contained the components corresponding to spots A, B, and G (G being unreacted glycine). Since A-1 and A-2 were the most easily crystallizable, much of the A component was removed by several crystallizations from mixtures of water and methanol. The resulting mother liquor was concentrated to give about 2 g. of syrupy solution and was streaked along an edge of several 25 X 57-cm. sheets of Whatman No. 3 MM paper and then chromatographed in the usual way (1). Reference strips 4 cm. wide were cut off from both sides of each sheet of paper and sprayed with ninhydrin. This treatment made possible the cutting off of that portion of spot B which did not overlap with spot A. The material containing spot B was extracted with methanol. After concentration and the addition of ether, 440 mg. of an amorphous white precipitate was obtained. This material was designated precipitate B. Eventually, B was found to be an impure sample of 2-deoxy-2-glycino-D-mannose.

An attempt was made in isolating components A and B from bread, using 35 loaves of bread each from 100 g. of flour with 1.0 g. of glycine incorporated in the baking formula (1). The same procedure used in the attempted isolation of 1-deoxy-1-glycino-D-fructose, described in the previous paper (1), was employed; and in the final paper-chromatographic separation, components A and B served as

reference spots. Small amounts (about 15 mg. each) of syrupy material with the same R_f values as A and B were obtained.

RESULTS AND DISCUSSION

The Basic Components from Reactions of Glycine with D-Fructose

Figure 1 shows some typical results for the 5N ammonium hydroxide (NH_4OH)-eluted basic components from the reaction of glycine-2-^{14}C with D-fructose. The resolution of the glycine-D-fructose interaction-products A and B, formed in the early stages of the reaction, is more apparent in the bottom chromatogram of Fig. 1, which was obtained with a longer development time (5 instead of 2 days). The $R_{glycine}$ values (R_f relative to that of glycine as 1.00) for components A and B were 0.50 and 0.58, respectively.

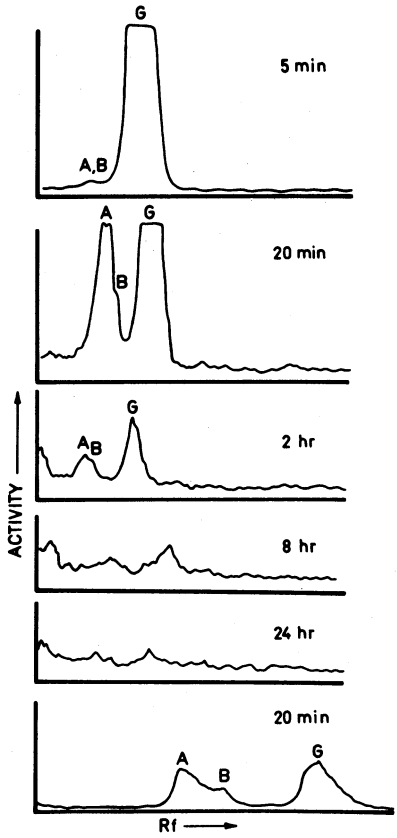
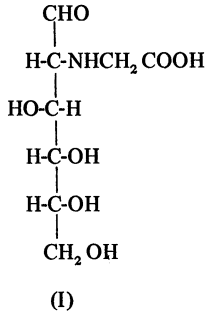


Fig. 1. Activity distributions on paper chromatograms of the basic components derived from heating glycine-2-^{14}C with D-fructose at 120°C. for various lengths of time; the presence of a third component, C, could be masked under the glycine peak G. The last 20-min. chromatogram was obtained with longer development time.

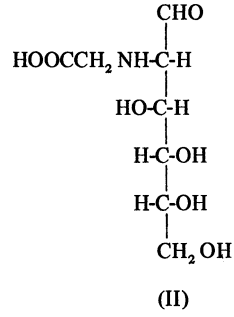
With a reaction time of 20 min., and using glycine-1-^{14}C instead of glycine-2-^{14}C, activity distributions similar to those shown in Fig. 1 were observed for the NH_4OH-eluted basic products. In the earlier work with active glycine and D-glucose (1), it was noted that when the elution of the basic components was carried out with 0.2N TCA instead of 5N NH_4OH, the glycine peak (G) did not appear, suggesting that glycine was not eluted by 0.2N TCA. In the present study, with a reaction time of 20 min., 0.2N TCA elution of the basic components from the reaction of glycine-2-^{14}C and D-fructose gave an active peak, to be designated component C, in the same region as the glycine peak G, besides peaks A and B. On the other hand, when the active reactant was glycine-1-^{14}C, the 0.2N TCA-eluted product did not show the active component C. Since TCA apparently could not elute glycine (1), and since it appeared only in the reaction with glycine-2-^{14}C and not with glycine-1-^{14}C, component C would appear to be some product of decarboxylation, masked under the large glycine peak. Although the exact nature of component C has not been ascertained, the present observations tend to lend further support to the previous conclusions (1-4) that Strecker-type of decarboxylation in Maillard browning reactions could take place after the amino acid has combined with the reducing sugar.

With reaction times of 2, 8, or 24 hr., the activity distributions shown in Fig. 1 appeared to be roughly similar to the corresponding behaviors in the reactions between glycine and D-glucose (1). These results may also be interpreted as before (1) as indicating that on longer heating, the initial interaction products would undergo further reactions, eventually giving rise to the less-mobile pigments, as suggested by the appearance of appreciable amounts of active material near the spot where the sample was originally applied.

From the reaction of glycine and D-fructose in absolute methanol, Heyns and co-workers (5) have isolated crystalline 2-deoxy-2-glycine-D-glucose (D-glucoseglycine) (I), which was also converted to its monohydrate, and 2-deoxy-2-glycino-D-mannose (D-mannoseglycine) (II) as an amorphous powder. Similarly, Anet (6) has reported I as the main product obtained from storing a concentrated solution of D-fructose and glycine at 50°C. for 38 days. Analogous to the Amadori rearrangement, I and II are rearrangement products (the Heyns rearrangement) formed from D-fructosylglycine, the initial condensation product of glycine and D-fructose (5).



(I)



(II)

Components A and B (Fig. 1) obtained in the present work were identified as the Heyns rearrangement products I and II, although only the crystalline material

A-2 isolated from the large-scale preparation was shown to be I free from impurities. Hydrolysis of components A or B in 2N HOAc in a sealed tube at 100°C. for 1 hr. gave, besides some unchanged material, paper-chromatographic spots corresponding to D-fructose and glycine, as was reported (5) both for I and for II. Further evidence for the identification of components A and B was based on the examination of the products obtained from the large-scale preparation using inactive glycine and D-fructose.

In the large-scale preparation, two batches of crystals with the same R_f value as component A, designated as A-1, m.p. 142° to 144°C. (decomp.), and A-2, m.p. 187° to 189°C. (charred), were obtained. Heyns and co-workers (5) reported that compound I began to char at 180°C. and did not completely melt at 250°C. These melting behaviors are somewhat different from those of A-1 and A-2. For comparison, glycine and D-fructose were allowed to react in absolute methanol, as described by Heyns and co-workers (5), and then the reaction mixture was worked up by the same procedure described earlier in this paper. The crystalline product corresponding to A-1 obtained from such a reaction in methanol turned out to be the monohydrate of I, m.p. 188° to 190°C. (charred); $[\alpha]_D^{20} = +78°$, lit. (5); $[\alpha]_D^{20} = +75°$. The analysis calculated for the monohydrate of I, $C_8H_{17}O_8N$, was C = 37.65; H = 6.71; and N = 5.49; that found was C = 37.73; H = 6.71; and N = 5.27. The original batch of A-1, obtained from "baking" the reactants on filter paper, melted at 142° to 144°C. (decomp.), $[\alpha]_D^{20} = +79°$, and it showed analysis of C = 39.92; H = 6.30; and N = 5.01. Apparently this batch of A-1 crystals from the model browning reactions was an impure sample of the monohydrate of compound I.

From the reaction of glycine and D-fructose in methanol (5), the crystalline product corresponding to A-2 that was obtained was the expected compound I. It melted at 188° to 190°C. (charred); $[\alpha]_D^{20} = +83°$, lit. (5); $[\alpha]_D^{20} = +81°$. The analysis calculated for I, $C_8H_{15}O_7N$, was C = 40.50; H = 6.37; and N = 5.82; that found was C = 40.67; H = 6.40; and N = 5.84. The original batch of A-2 crystals obtained from the model browning reaction showed essentially the same properties: m.p. 187° to 189°C. (charred), $[\alpha]_D^{20} = +83°$; and analysis gave C = 40.74; H = 6.41; and N = 5.82. These data suggest that crystalline A-2 was pure 2-deoxy-2-glycino-D-glucose (I).

The final proof of crystalline A-2 as 2-deoxy-2-glycino-D-glucose (I) was based on examination by nuclear magnetic resonance (NMR). Both A-2 and compound I prepared by the method of Heyns (5) showed identical NMR behaviors. Figure 2 shows the spectrum of A-2 taken within 10 min. after dissolution in deuterium oxide (D_2O) with a Varian HA-100 spectrometer. After the solution was allowed to stand at room temperature for 2 to 3 days, the spectrum obtained is that given in Fig. 3. The assignments of the appropriate absorptions to the various protons as shown in these figures were arrived at by spin decoupling, the different protons being designated as H_X, the subscript x indicating the carbon position in the D-glucose skeleton to which the proton is attached.

From the known NMR data relating to conformations and anomeric compositions of sugars in solution (7,8,9), the doublet at about τ4.0 is assigned to H_1 of the α-anomer. H_1 of the β-anomer, barely visible in Fig. 2 and more pronounced in Fig. 3, is also a doublet centered at about τ4.5. As shown in Fig. 2, the first-order coupling constants for $J_{\alpha H_1 H_2}$, $J_{H_2 H_3}$, $J_{H_3 H_4}$, and $J_{H_4 H_5}$,

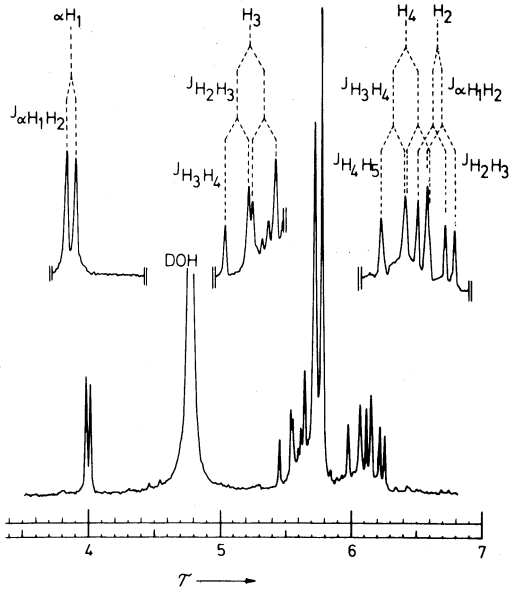


Fig. 2. NMR spectrum of 2-deoxy-2-glycino-D-glucose in D_2O recorded within 10 min. after dissolution (inserts drawn at expanded scale).

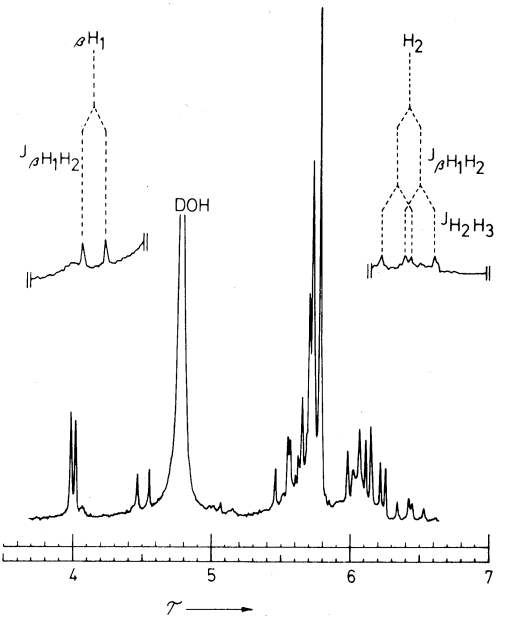
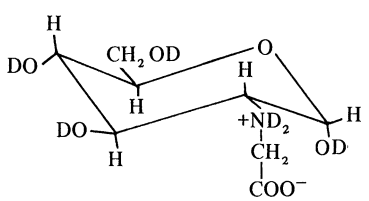
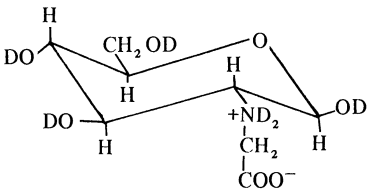


Fig. 3. NMR spectrum of 2-deoxy-2-glycino-D-glucose in D_2O recorded after reaching anomeric equilibrium (inserts drawn at expanded scale).

respectively, are about 3.5, 10.5, 9.0, and 8.5 Hz. As the solution of crystalline A-2 in D_2O is allowed to stand at room temperature, the NMR spectrum changes with time, finally reaching an equilibrium composition with the spectrum given in Fig. 3. Absorptions in addition to those in Fig. 2, attributable to the β-anomer, appeared. The βH_1 proton gives a doublet at τ4.5, with $J_{\beta H_1 H_2}$ of 8.5 Hz., and the H_2 quartet for the β-anomer appear in the τ6.4 region, with $J_{H_2 H_3}$ of 10.0 Hz. The above observations are consistent with the conclusion that crystalline A-2 initially existed as the cyclic α-anomer, 2-deoxy-2-glycino-α-D-glucopyranose with the C-1 conformation Ia (7,8,9). A solution of this compound in D_2O eventually gave an equilibrium mixture of the α- and β-anomers Ia and Ib (7,8,9) (the labile H atoms in structures Ia and Ib being replaced by deuterium atoms since the spectra were obtained in D_2O). From the relative areas of the αH_1 and βH_1 doublets in Fig. 3, the equilibrium composition is estimated to be consisting of 60% α- and 40% β-anomers.



Ia



Ib

Component B, isolated from the large-scale preparation as an amorphous precipitate, was deduced as an impure sample of 2-deoxy-2-glycino-D-mannose (II) on the basis of the following considerations. It has already been stated that hydrolysis of component B in 2N HOAc gave D-fructose and glycine as expected for II. For the amorphous compound II prepared by Heyns and co-workers (5), the reported $[\alpha]_D^{20} = -7°$, $[\alpha]_D^{20}$ found for precipitate B was -2°. This low specific rotation, although not identical with that reported for II, did suggest the probability of a close resemblance to II, since this value of $[\alpha]_D^{20}$ was quite different from that of D-glucoseglycine I (+83°) or that of D-fructoseglycine (-65°) obtained in the reaction of glycine with D-glucose (1). The NMR spectrum of precipitate B was also examined. This spectrum, although too complex for a complete first-order assignment of all the proton absorptions, did show absorptions for the α- and β-anomeric protons whose small coupling constants (about 1.0 to 1.5 Hz.) were very similar to those reported for D-mannose (8), suggesting the presence of the D-mannose structure in component B. It was, therefore, concluded that the amorphous precipitate B, obtained in the large-scale browning reaction between glycine and D-fructose, was an impure sample of 2-deoxy-2-glycino-D-mannose (II).

Finally, in the attempted isolation of components A and B from 35 loaves of bread baked with added glycine, small amounts of syrupy material, each weighing about 15 mg., with the same R_f values as A and B, were obtained. These syrups, on hydrolysis with 2N HOAc, did give chromatographic spots corresponding to

D-fructose and glycine, suggesting the probability that under the baking conditions employed, only very minute amounts of the Heyns rearrangement products I and II could survive in the finished bread.

Changes with Heating Time in the Activities of Various Fractions from Reactions between Glycine and D-Fructose

Variations with lengths of heating time at 120°C. in the radioactive contents of the volatile, basic water-soluble, nonbasic water-soluble, and water-insoluble fractions from the reaction of glycine-2-^{14}C or glycine-1-^{14}C with D-fructose, or from heating the basic components (chiefly compounds I and II) derived from the reaction of glycine with uniformly labeled D-fructose-^{14}C, are summarized in Tables I, II, and III. The analogous data obtained from the study with glycine and D-glucose (1) are also given in these tables for the purpose of comparison.

On examination of the data for the reactions of glycine with D-fructose and with D-glucose in Tables I, II, and III, it can be seen that although there are differences in the actual percentages of activity found in the various fractions, the general trends of behavior are similar. The most consistent difference appeared to be a less-rapid loss of ^{14}C-activity as volatile materials in the reaction of glycine-1-^{14}C with D-fructose than in the analogous reaction with D-glucose (Table II). Correspondingly, the activity remaining in the basic water-soluble fraction, up to a reaction time of 8 hr., was found to decrease less rapidly in the reaction between glycine-1-^{14}C with D-fructose than with D-glucose (Table II). The data in Table III also suggest that the loss of volatile materials derived from the D-fructose moiety of the basic interaction products of glycine and D-fructose appeared to be initially more rapid than the analogous loss of volatiles from the D-glucose moiety of the basic products from the interaction of glycine with D-glucose. Such

TABLE I. RADIOACTIVITY IN VARIOUS FRACTIONS FROM HEATING OF GLYCINE-2-^{14}C WITH D-FRUCTOSE[a]

Time of Heating	Activity Contents, %[b]			
	Volatile	Basic Water-Soluble	Nonbasic Water-Soluble	Water-Insoluble
5 min.	0 (0)	83.6 (80.9)	4.2 (6.0)	0.5 (1.0)
10 min.	0 (0)	77.4 (74.9)	8.3 (10.7)	1.8 (1.3)
15 min.	0 (0)	69.1 (67.5)	12.4 (18.2)	6.3 (2.2)
20 min.	0 (0)	62.8 (62.3)	17.8 (20.7)	7.0 (9.5)
30 min.	0 (0)	59.2 (56.1)	19.0 (23.2)	8.0 (10.4)
45 min.	0 (0)	55.0 (51.3)	20.9 (26.0)	9.2 (11.9)
1 hr.	0 (0)	49.2 (49.8)	24.1 (24.6)	16.3 (12.9)
2 hr.	0 (0)	46.8 (47.0)	21.3 (22.9)	19.4 (14.8)
4 hr.	0 (0)	43.8 (42.7)	21.9 (27.0)	21.3 (18.0)
8 hr.	0 (0)	37.1 (38.4)	20.6 (24.8)	29.5 (26.1)
24 hr.	0 (0)	33.6 (33.4)	21.8 (26.7)	33.6 (29.3)
48 hr.	0 (0)	24.4 (21.7)	24.2 (25.5)	41.3 (40.8)

[a]Analogous data from Ref. 1 for the heating of glycine-2-^{14}C with D-glucose are given in parentheses.

[b]In this and subsequent tables, the original activity on the paper disc before heating was taken as 100%. In most cases, the total recovery of activities in the four fractions was less than 100%. This could be due to losses of uneluted material remaining in the ion-exchange column or to losses arising from manipulation of the samples prior to the counting of the basic and nonbasic water-soluble fractions, or both.

TABLE II. RADIOACTIVITY IN VARIOUS FRACTIONS FROM HEATING OF GLYCINE-1-^{14}C WITH D-FRUCTOSE[a]

Time of Heating	Activity Contents, %			
	Volatile	Basic Water-Soluble	Nonbasic Water-Soluble	Water-Insoluble
5 min.	0 (0)	81.8 (83.0)	7.0 (10.6)	0.8 (1.6)
10 min.	0 (0.6)	78.6 (73.1)	12.4 (16.0)	1.4 (1.8)
15 min.	6.2 (11.5)	59.1 (53.4)	16.8 (18.3)	2.4 (2.5)
20 min.	11.3 (19.6)	49.1 (45.6)	18.5 (20.6)	2.6 (2.8)
30 min.	20.5 (25.4)	41.2 (37.8)	16.9 (17.2)	3.2 (3.0)
45 min.	26.4 (31.5)	31.8 (28.8)	17.6 (16.3)	4.0 (3.2)
1 hr.	33.8 (38.5)	23.8 (25.6)	19.4 (19.0)	4.8 (5.2)
2 hr.	45.8 (53.1)	21.9 (21.4)	20.0 (19.0)	5.7 (4.4)
4 hr.	58.4 (64.3)	19.0 (15.4)	17.6 (13.9)	6.5 (4.9)
8 hr.	67.8 (69.0)	14.4 (12.8)	15.2 (12.7)	10.0 (6.8)
24 hr.	68.0 (71.5)	8.8 (9.5)	12.0 (11.8)	13.2 (8.6)
48 hr.	66.9 (73.2)	6.9 (8.3)	11.1 (10.9)	15.0 (12.1)

[a]Analogous data from Ref. 1 for the heating of glycine-1-^{14}C with D-glucose are given in parentheses.

TABLE III. RADIOACTIVITY IN VARIOUS FRACTIONS FROM HEATING OF THE BASIC COMPONENTS, CHIEFLY 2-DEOXY-2-GLYCINO-D-GLUCOSE AND 2-DEOXY-2-GLYCINO-D-MANNOSE, DERIVED FROM GLYCINE AND D-FRUCTOSE-^{14}C[a]

Time of Heating	Activity Contents, %			
	Volatile	Basic Water-Soluble	Nonbasic Water-Soluble	Water-Insoluble
5 min.	0 (0)	66.7 (63.4)	20.8 (21.4)	0.3 (0.5)
10 min.	0.9 (0.3)	62.2 (56.3)	32.1 (22.4)	1.3 (0.8)
15 min.	1.9 (0.5)	58.9 (50.2)	30.6 (18.3)	1.4 (1.3)
20 min.	2.9 (0.7)	45.5 (44.8)	30.0 (20.1)	1.5 (1.2)
30 min.	3.7 (1.1)	32.9 (38.6)	29.2 (22.4)	3.0 (3.3)
45 min.	3.8 (1.7)	22.8 (29.3)	29.4 (20.6)	3.3 (4.0)
1 hr.	3.9 (2.0)	21.7 (25.8)	25.4 (31.9)	4.3 (3.8)
2 hr.	4.9 (2.3)	19.3 (23.4)	23.7 (24.7)	9.9 (5.9)
4 hr.	7.8 (5.8)	17.8 (20.2)	25.5 (33.7)	12.1 (9.0)
8 hr.	8.5 (9.8)	16.8 (15.3)	22.1 (32.0)	16.0 (13.7)
24 hr.	10.1 (11.6)	15.4 (13.9)	32.1 (29.2)	26.1 (23.0)
48 hr.	11.1 (12.7)	13.8 (10.5)	27.5 (31.2)	32.3 (33.4)

[a]Analogous data from Ref. 1 for the heating of the basic components, chiefly 1-deoxy-1-glycino-D-fructose, derived from glycine and D-glucose-^{14}C, are given in parentheses.

differences do indicate variations in certain reaction rates as well as in the details of the processes involved. On the other hand, the overall similarity in the trends of behavior would suggest the general similarity in the Maillard-type of browning reactions of glycine with D-fructose or with D-glucose. The qualitative conclusions presented previously in the study with glycine and D-glucose (1), such as the formation of basic water-soluble materials in the initial stages of reaction, the inclusion of the products of the intermediate stages in the nonbasic water-soluble fraction, and the formation of polymeric water-insoluble materials in the final stages, as well as the major importance of Strecker-type of decarboxylation in

accounting for the loss of activity from glycine-1-^{14}C, could be equally well applied to the present results obtained from studies with glycine and D-fructose.

An interesting difference has been noted in the behavior of glycine-2-^{14}C in the baking studies and in the model reactions. No volatile ^{14}C-material was found when model reactions between glycine-2-^{14}C and D-glucose or D-fructose were carried out. On the other hand, when glycine-2-^{14}C was incorporated into the baking formula during the making of bread (4), some of the ^{14}C-activity appeared in the volatile fractions, indicating that the C-2 carbon of glycine could undergo more complex transformations under the conditions of actual breadmaking. It is, of course, to be expected that an amino acid, such as glycine, would have the opportunity of taking part in a greater number of reactions in actual breadmaking, such as reactions with the products of fermentation, which are not available in the model reaction studies.

Acknowledgment

The financial support given by the National Research Council of Canada is gratefully acknowledged.

Literature Cited

1. LEE, C. C., and LIAU, Y. H. Studies with radioactive tracers. XVII. Model browning reactions between glycine and D-glucose. Cereal Chem. 48: 238 (1971).
2. HODGE, J. E. Chemistry of browning reactions in model systems. J. Agr. Food Chem. 1: 928 (1953).
3. LIAU, Y. H., and LEE, C. C. Studies with radioactive tracers. X. The fate of glycine-1-^{14}C during breadmaking. Cereal Chem. 43: 706 (1966).
4. LIAU, Y. H., and LEE, C. C. Studies with radioactive tracers. XVI. The fate of glycine-2-^{14}C during breadmaking. Cereal Chem. 47: 404 (1970).
5. HEYNS, K., BREUER, H., and PAULSEN, H. Darstellung und Verhalten der 2-N-Aminosäure-2-deoxy-glucosen ("Glucose-aminosäuren") aus Glycin, Alanin, Leucin und Fructose. Chem. Ber. 90: 1374 (1957).
6. ANET, E. F. L. Chemistry of non-enzymic browning. II. Some crystalline amino acid-deoxy-sugars. Aust. J. Chem. 10: 193 (1957).
7. ANGYAL, S. J. The composition and conformation of sugars in solution. Angew. Chem. Int. Ed. Engl. 8: 157 (1969).
8. MACKIE, W., and PERLIN, A. S. Pyranose-furanose and anomeric equilibria, influence of solvent and of partial methylation. Can. J. Chem. 44: 2039 (1966).
9. HORTON, D., JEWELL, J. S., and PHILIPS, K. D. Anomeric equilibria in derivatives of amino sugars. Some 2-amino-2-deoxy-D-hexose derivatives. J. Org. Chem. 31: 4022 (1966).

[Received September 27, 1971. Accepted February 7, 1972]