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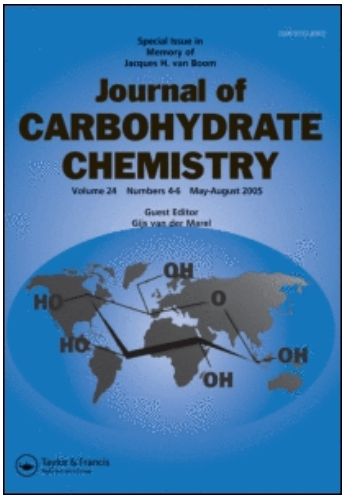

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Maillard Polymers Derived from D-Glucose-1 and -6-^{14}C, Glycine-1 and -2-^{14}C, and C-1-, and Methyl-^{14}C Methionine

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MAILLARD POLYMERS DERIVED FROM D-GLUCOSE-1 AND -6-^{14}C, GLYCINE-1 AND -2-^{14}C, AND, C-1-, AND METHYL-^{14}C METHIONINE [1]

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ABSTRACT

Maillard polymers were prepared from D-glucose-1 and -6-14C, glycine-1 and -2-^{14}C, as well as C-1 and methyl-^{14}C methionine, and the activities of the isolated polymers measured as a function of time. In both cases, C-1 of the amino acids were incorporated at the lowest levels, with D-glucose carbon atoms at the highest levels. The data support the conclusions that carbon dioxide, produced during the Maillard reaction, arises from C-1 of the amino acids, but also suggests that other carbons of the amino acids may contribute as well.

INTRODUCTION

The reaction of reducing sugars with amino acids or protein to produce brown polymers was originally described by Maillard.[2]

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The Maillard reaction, since the original report, has been the subject of numerous studies, and, more recently, several symposia have been held on the subject.[3,4] The exact origin and constitution of Maillard polymers are not, at present, well understood. Substantial information is available on the early phase of the reaction.[5] Initially an aldose reacts with an amino acid to give a 1-amino-1-deoxy-2-ketose (Amadori compound). Amadori compounds[6] are known to undergo dehydration in acidic solution (with loss of the amine substituent) to give dicarbonyl intermediates, 2-furaldehydes and other reactive molecules. Such compounds probably contribute to polymer formation. Furthermore, the amino acid may undergo Strecker-type degradations to give carbon dioxide and reactive aldehydes, thus resulting in transamination reactions.

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Recently in this laboratory,[7] Maillard polymers arising from the reaction of D-glucose, glycine, and methionine were prepared and studied. The results suggest that the polymer contains (in part) the amino acid carbons (as evidenced by ^{13}C NMR), nitrogen (derived from the amino acid) and carbon atoms derived from the sugar. Elemental analyses show that the polymers correspond in empirical formula to sugar plus amino acid minus about three moles of water.

In his early papers, Maillard[2] observed CO_2 production during the reaction and, since that time, its origin has been the subject of several studies. Wolfrom and co-workers,[8] using a D-glucose-glycine-1-^{14}C system, collected the $^{14}CO_2$ during the reaction and concluded that the CO_2 evolved was almost entirely derived from the carboxyl group of glycine. On the other hand, Stadtman and co-workers[9] found (using similar experimental techniques) that appreciable quantities of CO_2 from sugar sources were present in the evolved CO_2.

While the experimental techniques used in the above studies were simple and straightforward, they gave conflicting results and, furthermore, provide no information relative to carbon atoms that are actually incorporated into the polymer. This paper reports some radiochemical data on Maillard polymers prepared

using, respectively, D-glucose-1- and -6-^{14}C, as well as glycine -1 and -2-^{14}C, and C-1 and methyl -^{14}C methionine.

EXPERIMENTAL

Materials and Methods. Radioactive D-glucose-1 and -6-^{14}C, and amino acids were obtained from Amersham Corporation, Arlington Heights, Illinois. The ^{14}C-labeled starting materials all had a specific activity of approximately 50 mCi/mmol and were dissolved in 0.25 mL of water. Prior to use the samples were diluted to about 5.0 mL with phthalate buffer. Radioactive samples were counted by combustion, using a Packard model 306 ozidizer. The $^{14}CO_2$ was collected in Carbasorb and then counted using a Beckman scintillation counter.

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Preparation of ^{14}C Labeled Maillard Polymers. The experimental procedure was the same for each experiment. To a 50-mL round bottomed flask was added 4.5 g. (0.025 moles) of D-glucose, 0.025 moles of amino acid, and 10.0 μCi of isotopically labeled sugar or amino acid (in 1 mL of phthalate buffer, pH 3.5). An additional 24 mL of buffer was added, and the solution was brought to reflux. At the end of the reaction time, the contents of the flask were transferred to a dialysis bag (nominal molecular weight cutoff = 6,000 - 8,000 daltons), dialyzed for two days against 1 L of water (2 changes), and then against running tap water for five days. The solution containing the non-dialyzable Maillard polymer was then freeze dried, and a 10-mg sample was combusted and counted.

RESULTS AND DISCUSSION

The collected data are presented graphically in Figure 1 (for a reaction involving glycine) and Figure 2 (for a reaction involving methionine).

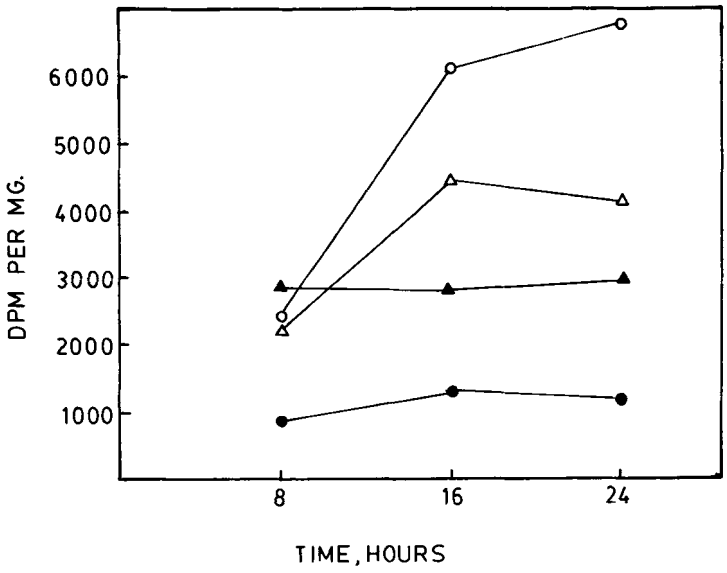

Fig. 1. Radiochemical activities of polymers prepared from, D-glucose-6-^{14}C (○), -1-^{14}C (△) and glycine-1-^{14}C (●), -2-^{14}C (▲) as a function of reaction time.

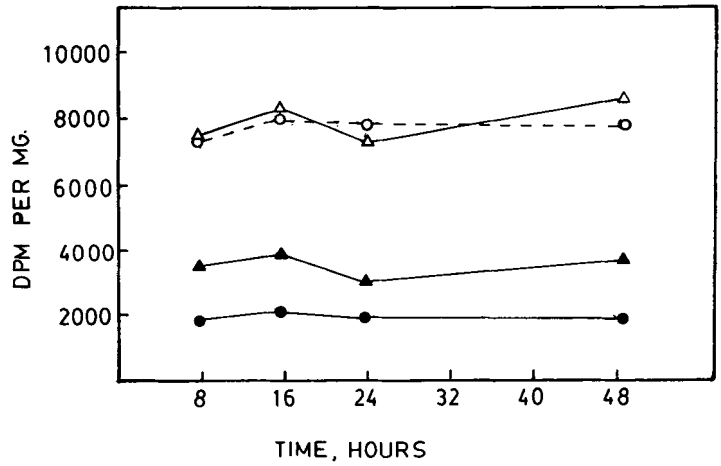

Fig. 2. Radiochemical activities of polymers prepared from D-glucose-6-^{14}C (○), -1-^{14}C (△) and methionine -1-^{14}C (●), -methyl -^{14}C (▲) as a function of reaction time.

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The data suggest that the polymerization reaction is very complex. In both cases, the carboxyl carbon of the amino acid is incorporated at the lowest levels. This supports previous suggestions,[10,11] that a Strecker degradation may be a feature of such reactions and supports the conclusions that this carbon is a major contributor of evolved CO_2 in such reactions. Holtermand[12] conducted experiments relative to whether Strecker degradations occur during the Maillard reactions and, in some cases, was able to detect aldehydes resulting, presumably, from the decarboxylation of amino acids. He was not, however, able to detect formaldehyde in reactions involving glycine and did not include methionine in his studies. The fact that, in both cases, both of the labeled amino acid carbon atoms are incorporated at substantially lower levels than those of the sugar is also noteworthy. This is also consistent with a Strecker degradation occurring, which would release C^{14}-labeled volatile aldehydes, some of which could escape from the reaction and thus not be completely incorporated into the polymer.

It is clear from prior studies as well as from these data that the formation of Maillard polymers probably involves a multiplicity of reactions and that Strecker degradations could well be a feature of such degradations.

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