

CHEMICAL INTERACTIONS OF AMINO COMPOUNDS AND SUGARS. VI.¹ THE REPEATING UNIT IN BROWNING POLYMERS²

Sir:

Individual browning reactions were effected between glycine and each of the radioactive sugars L-arabinose-1-C¹⁴, D-xylose-1-C¹⁴, and D-glucose-1-C¹⁴, as well as between each of these sugars in their inactive forms and glycine-1-C¹⁴ and glycine-2-C¹⁴, respectively. The aqueous solutions, 0.125 M in sugar and 1.25 M in glycine, were heated under a nitrogen stream at 95° (short of reflux) for 90 hr. and the evolved carbon dioxide was collected as barium carbonate. The polymer selected for study was the water-soluble, non-dialyzable, brown solid fraction¹ obtained in 20-45% yields by dialysis, using a cellulose membrane, followed by concentration, precipitation with dioxane and drying under reduced pressure (0.5 mm.) at 56° for 20 hr. Elementary analyses were carried out on the polymers. The observable specific activities³ of the polymers and of the radioactive reactants were used to calculate the relative number of each type of labeled carbon atom in the polymers and also the percentage recovery of the sugar number-one carbons in the polymers. The amount of barium carbonate arising from the glycine carbons was calculated from the activities of "infinitely-thick" plates, employing an experimentally determined factor relating these activities to the glycine activities. The amounts of carbon dioxide arising from the sugar number-one carbons were calculated from the maximum specific activities of the barium carbonate and of the sugar samples.

In agreement with Mackinney and co-workers,⁴ who employed uniformly labeled D-glucose and glycine-1-C¹⁴, we find that essentially all (90-

100%) of the carbon dioxide formed originated in the glycine carboxyl group. The ratio of sugar number-one carbon:glycine methylene carbon:nitrogen was established as 1:1:1 in all of our polymers. The empirical formulas, relative to the glycine methylene group, were calculated and found to be C_{6.0}H_{6.4}O_{2.0}N_{1.0}(CH₂)(CO₂H)_{0.5} for the glycine reaction product from D-glucose and C_{5.0}H_{4.7}O_{1.5}N_{0.8}(CH₂)(CO₂H)_{0.8} for each of the products from the two pentoses. The pentose-glycine polymers were essentially identical. All three polymer fractions appeared to have arisen from an equimolar reaction between the reducing sugar and the amino acid effected without apparent carbon chain scission of the sugar, with partial decarboxylation of the amino acid, and with nearly complete trimolar dehydration of the sugar. The repeating unit for the D-glucose-glycine polymer very closely approximates C₆H₆O₂N(CH₂)(CO₂H)_{0.5} while that for the pentose-glycine polymers approximates C₆H₄ON(H₂O)_{0.5}(CH₂)(CO₂H)_{0.8}.

Illustrative of the method used in deriving these formulas, the reaction of D-glucose-1-C¹⁴ (630 counts/min./mg.) and glycine yielded a polymer (610 counts/min./mg.) of analysis: C, 56.17; H, 5.60; N, 8.87. The dilution factor (D. F.) was then: D. F. = (count on polymer) (%C of reactant in labeled position)/(count on active sugar) (%C in polymer) = 0.115. Two more D. F. values, 0.060 and 0.127, were obtained from the reaction of D-glucose with glycine-1-C¹⁴ and glycine-2-C¹⁴, respectively. Combination of these values with the empirical formula C_{7.40}H_{8.78}NO_{2.90} and adjustment to unit glycine methylene carbon gave: CH₂, 1; CO₂H, 0.47; C from C₁ of D-glucose, 0.91; total C from D-glucose, 6.00; total polymer C, 7.47; N, 1.01; H, 8.86; O, 2.93; and thus C_{6.00}-H_{6.39}O_{2.01}N_{1.01}(CH₂)(CO₂H)_{0.47}.

These repeating units approach the sugar dehydration stage represented by a 2-furaldehyde-glycine condensation product, for the pentose system, and by a 5-(hydroxymethyl)-2-furaldehyde-glycine condensation product for that from the hexose, but do not require that the furan rings are necessarily present in their intact cyclized forms.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

M. L. WOLFROM
R. C. SCHLICHT
A. W. LANGER, JR.
C. S. ROONEY

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(4) F. H. Stadtman, C. O. Chichester and G. Mackinney, *THIS JOURNAL*, **74**, 3194 (1952); C. O. Chichester, F. H. Stadtman and G. Mackinney, *ibid.*, **74**, 3418 (1952).