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Note

β-D-Glucopyranosylamine and 2-amino-2-deoxy-D-glucose from ultraviolet irradiation of D-glucose and amino acids*

LANDIS W. DONER, ROMAN BALICKI, AND ROY L. WHISTLER*
Department of Biochemistry, Purdue University, Lafayette, Indiana 47907 (U. S. A.)
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In preliminary work to determine compounds that might be formed when a solution of D-glucose and amino acids is subjected to ultraviolet radiation, we examined several products obtained when L-lysine and glycine are the amino acids.

From the earliest work on the photolysis of D-glucose it is known that acids are produced and that carbon dioxide, hydrogen, and, perhaps, some carbon monoxide are formed[1]. Phillips[2,3] observed that carbon dioxide was continuously released during D-glucose photolysis. D-Arabinose is detected rather early in the photolysis reaction[4], but D-gluconic acid is observed[4] after a period of photolysis. Amino acids liberate ammonia in differing amounts with L-lysine producing 21% and glycine producing 9% from the total nitrogen during a 2-h photolysis period[5,6].

In the present work, a solution of D-glucose and amino acid was subjected to unfiltered irradiation from a low-pressure mercury lamp. Because of the high polarity of the photoproducts, they were converted into their peracetylated derivatives, thus making them more amenable to chromatographic separations. Mild acetylation conditions using pyridine as a catalyst at 25° were unsuitable for blocking all hydroxyl and amino groups in the products, but sodium acetate as a catalyst and elevated temperatures resulted in complete acetylation.

Photolysis of D-glucose with L-lysine and glycine resulted in the production of a large number of chromatographically observed photoproducts; but most of them in very small amounts. Some of these products derived from photolysis of the sugar, some from photolysis of the amino acid, and others from the combination of carbohydrate and amino acid or carbohydrate and amino acid fragments.

Regardless of the amino acid used, large amounts of starting D-glucose could be isolated unreacted, as its pentaacetate, at the end of a 72-h photolysis period. Amino acids are more readily decomposed photochemically than are the carbohydrates, and no acetylated amino acid was present when the reactions were completed.

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After crystallization of D-glucose pentaacetate from the acetylated reaction mixture, silica gel column-chromatography yielded more D-glucose pentaacetate in the first-eluted fraction. The second-eluted fraction contained only *N*-acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine, which was crystallized and characterized. It was the major product of the photoreaction and amounted to 2.5% in the D-glucose–L-lysine reaction, but was obtained in only 0.18% yield from the D-glucose–glycine reaction. Since β-D-glucopyranosylamine must result from D-glucose combining with ammonia liberated from photolysis of the amino acid, the highest yields would be expected from the reaction containing L-lysine, since this amino acid produces more ammonia in photolysis than does glycine.

The third component eluted on silica gel chromatography of the L-glycine reaction mixture was 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucopyranose obtained in 0.44% yield. Although the mechanism for its formulation has not been developed, the most likely route would follow the Heyns[7] rearrangement.

From both reaction-mixtures, subsequent chromatographic fractions were obtained in very low yield, and mass-spectral data indicated that several fractions contained an intact D-glucopyranose ring with various fragments of the amino acid linked to the anomeric carbon atom.

EXPERIMENTAL

General methods. — Irradiations with unfiltered u.v. light were conducted with a Hanovia 450-W mercury lamp (769A36) inserted into a water-cooled, quartz immersion-well. The purity of products and course of reactions were monitored by t.l.c. on 5 × 13 cm plates coated with Silica Gel G type 60 (Merck, Darmstadt). Compounds were located by spraying with 5% sulfuric acid in ethanol and heating until permanent char spots were visible. Column chromatography was conducted on silica gel (T. G. Baker Chemical Company, Phillipsburg, New Jersey). Melting points were measured on a Fisher–Johns apparatus and are corrected. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter at 25°.

Irradiation of a D-glucose and L-lysine mixture. — A solution of D-glucose (6.16 g) and L-lysine (5.00 g) in water (200 ml) was irradiated for 72 h while nitrogen was bubbled through the solutions and the temperature maintained below 5°. Water was removed by lyophylization, and the dark syrup obtained was acetylated by heating to 90° with acetic anhydride (120 ml) and sodium acetate (6.0 g). After 12 h, the mixture was poured into ice–water (400 ml) and kept for 12 h. After extraction of the solution with three 400-ml portions of chloroform and washing the extracts with a saturated aqueous solution of sodium hydrogencarbonate, removal of the chloroform under reduced pressure yielded 17 g of syrup. D-Glucose pentaacetate (7.8 g) was crystallized from the mixture when it was dissolved in 150 ml of ether and stored overnight in the refrigerator. After filtration and removal of ether from the filtrate under reduced pressure, the syrup obtained was fractionated by elution from a silica gel column with 15:1 (v/v) benzene–methanol. Residual D-glucose pentaacetate

was eluted first, followed by *N*-acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (320 mg, 2.5% based on D-glucose), m.p. 163–164°, $[\alpha]_D^{25}$ +24.3° (*c* 2.0, chloroform); lit.[8]: m.p. 163–164°, $[\alpha]_D$ +17.4°.

Anal. Calc. for $C_{16}H_{23}NO_{10}$: C, 49.36; H, 5.91; N, 3.60. Found: C, 49.27; H, 5.73; N, 3.63.

Irradiation of a D-glucose and glycine mixture. — A solution of D-glucose (27 g) and glycine (17.1 g) in water (900 ml) was irradiated for 72 h, lyophylized, and acetylated, and most of the D-glucose pentaacetate removed by crystallization (47.66 g), as just described. After evaporation of ether from the mother liquor, the syrup was chromatographed on silica gel to give D-glucose pentaacetate (320 mg), followed by *N*-acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (19 mg, 0.18% based on D-glucose), m.p. 163–164°, $[\alpha]_D^{25}$ +24.3° (*c* 2.0, chloroform). A third eluate fraction produced 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (46 mg, 0.44%), m.p. 139–140°, $[\alpha]_D^{25}$ +86.5° (*c* 1.0, chloroform); lit.[9]: m.p. 133°, $[\alpha]_D$ +93.5° (chloroform).

Anal. Calc. for $C_{16}H_{23}NO_{10}$: C, 49.36; H, 5.91; N, 3.60; mol. wt.: 389. Found: C, 49.26; H, 5.91; N, 3.28; mol. wt. 261 (m.s.).

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