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Note

The formation of 2-deoxy-D-arabino-hexono-1,4-lactone from D-glucose by γ-radiolysis

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γ-Radiolysis of aqueous solutions of carbohydrates results in decomposition because of a secondary action of the radiolysis products of water[1], and many products have been found[2–6]. Some deoxy compounds, namely, malonaldehyde[7–9] and 2-deoxy sugars[9,10], are formed from several sugars and sugar alcohols, and a 5-deoxyhexos-4-ulose was formed from methyl α-D-glucopyranoside[11]. The mechanism of formation of deoxy compounds has been postulated to involve the hydrated electron[8,10,11] (e_{aq}^{-}), produced by radiolysis of water, and initiation by hydrogen abstraction from the sugar by the hydroxyl radical[9,12,13].

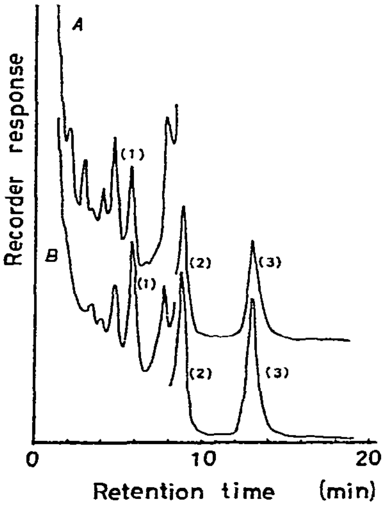

Fig. 1. G.l.c. separation of the γ-radiolysis products of D-glucose, as their trimethylsilyl ethers: *A*, aeration during irradiation; *B*, deaeration with nitrogen before irradiation. 1, 2-Deoxy-D-*arabino*-hexono-1,4-lactone; 2, α-D-glucose; 3, β-D-glucose.

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*The editors regret the delay in the acceptance of this Note, which was caused by an administrative error.

This note reports the isolation and identification of 2-deoxy-D-*arabino*-hexono-1,4-lactone formed on irradiation of aqueous solutions of D-glucose.

When an aqueous solution of D-glucose (10mM) was γ-irradiated with 2.0 Mrad in the absence and presence of oxygen, many products could be subsequently detected by g.l.c. of the freeze-dried and *O*-trimethylsilylated sample (Fig. 1). In a larger scale experiment, 50mM D-glucose was irradiated, and after removal of unchanged D-glucose, two products were isolated by repeated column chromatography and identified (see Experimental) as methyl 2-deoxy-D-*arabino*-hexonate (**1**) and 2-deoxy-D-*arabino*-hexono-1,4-lactone (**2**).

Hydrolysis of **1** with methanolic ammonia, followed by dehydration of the product, gave **2**, a known compound[14]. Peak 1 in g.l.c. (Fig. 1) corresponded to **2**; **1** was not produced directly from D-glucose during γ-radiolysis but was formed by methanolysis of **2** during the isolation procedure.

Although D-gluconic acid and 2-deoxy-D-*arabino*-hexose (2-deoxy-D-glucose) are known products of the radiolysis of D-glucose, the formation of 2-deoxy-D-*arabino*-hexono-1,4-lactone has not hitherto been observed. Studies of the mechanism of formation of this lactone are in progress.

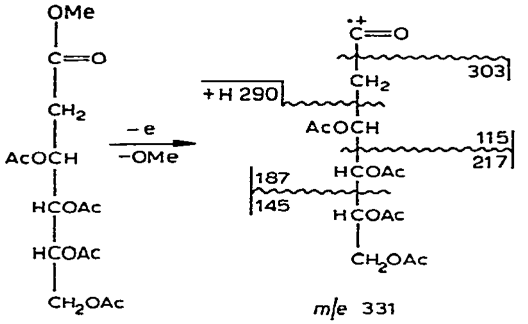
EXPERIMENTAL

Irradiation. — Aqueous solutions of D-glucose, which were severally deaerated with nitrogen and aerated, were irradiated with 2.0 Mrad at 20°, using γ-rays from a ^{60}Co source (4000 Ci). Solutions were prepared with triply distilled water.

G.l.c. — Irradiated 10mM D-glucose (3 ml) was freeze-dried, the residue was dissolved in anhydrous pyridine (1 ml), hexamethyldisilazane (0.4 ml) and chlorotrimethylsilane (0.2 ml) were added, and the mixture was heated at 70° for 10 min. G.l.c. of the trimethylsilylated product mixture was carried out on a Hitachi chromatograph Model K53 fitted with a flame-ionization detector and a stainless-steel column (0.3 x 100 cm) containing 5% OV-1 on 80–100 mesh Chromosorb W. The nitrogen flow-rate was 30 ml/min, and the column and injection temperatures were 185° and 280°, respectively.

Isolation of the radiolysis products. — A deaerated 50mM solution (10 l) of D-glucose was irradiated and then concentrated (to ~500 ml) under reduced pressure below 40°. Methanol (2 l) was added to the concentrate and the mixture was refrigerated overnight. The D-glucose which separated was removed, and the filtrate was concentrated under reduced pressure to give a syrupy residue (21 g) which was eluted from silica gel (500 g) with ethyl acetate–methanol (4:1); 50-ml fractions were collected. The product (~150 mg), isolated from fractions 24–30, was recrystallised from methanol–ethyl acetate to give methyl 2-deoxy-D-*arabino*-hexonate (**1**) as plates, m.p. 147–148°, $[\alpha]_D^{20}$ +9.2° (*c* 1.1, methanol); ν_{max}^{KBr} 3300 (OH) and 1727 cm^{-1} (ester) (Found: C, 43.80; H, 7.28. $C_7H_{14}O_6$ calc.: C, 43.29; H, 7.27%). Treatment of **1** with acetic anhydride and pyridine gave a treta-acetate **3**, m.p. 59–60°, $[\alpha]_D^{20}$ +34.7° (*c* 0.3, chloroform); ν_{max}^{KBr} 1740 and 1215 cm^{-1} (Ac) (Found: C, 49.55; H, 5.71.

$C_{15}H_{22}O_{10}$ calc.: C, 49.72; H, 6.21%). N.m.r. data (100 MHz, chloroform-*d*, internal tetramethylsilane): δ 2.02, 2.06, 2.10, and 2.15 (*s*, 4Ac), 2.57 (2 protons, $-C-CH_2-CO-$), 3.70 (*s*, 3 protons, $COOCH_3$), 4.22 (2 protons, $-C-CH_2-OCO-$), ~5.32 (*m*, 3 protons $-C-CH-OCO-$). Mass spectrum: *m/e* 331 (M^+-31, 27%), 303 (10), 290 (73), 217 (80), 187 (70), 145 (73), 115 (70), and 43 (base peak). The origin of these peaks is shown below.



3 (mol. wt. 362)

The residue from fractions 24–30, after removal of **1**, was rechromatographed on silica gel (60 g) with ethyl acetate–methanol (9:1). A crystalline product was obtained from fractions 32–38, which appeared homogeneous on g.l.c. and t.l.c. Recrystallisation from methanol–ethyl acetate gave 2-deoxy-D-*arabino*-hexono-1,4-lactone (**2**) as plates (52 mg), m.p. 95–96°, $[\alpha]_D^{25}$ +73° (*c* 0.5, water); ν_{max}^{KBr} 3400 (OH) and 1774 cm^{-1} (γ-lactone) (Found: C, 44.10; H, 5.98. $C_6H_{10}O_5$ calc.: C, 44.44; H, 6.22%); lit.[14] m.p. 95–97°, $[\alpha]_D^{21}$ +68°.

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