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Preliminary communication

Deoxy sugars produced by γ-irradiation of hexoses in oxygen-free, aqueous solution

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2-Deoxy-D-*arabino*-hexono-1,4-lactone is formed[1] by γ-radiolysis of D-glucose, and the presence of other, unidentified, deoxy sugars in irradiated sugar solutions has been suggested by Scherz[2]. We now report on deoxy sugars formed as main products when solutions of D-glucose and D-fructose were irradiated under oxygen-free conditions.

Solutions (10–20 mM) of D-glucose and D-fructose, prepared with triply distilled water, were deoxygenated with nitrogen gas and irradiated (2.0 Mrad) at 20° with γ-rays from a ^{60}Co source (4 KCi). The solutions were then treated with an excess of sodium borohydride, and the resulting sugar alcohols were acetylated (acetic anhydride–sulphuric acid) and subjected to g.l.c. (Fig. 1). The following peaks were identified on the basis of retention times: G-3 and F-3 (erythritol tetra-acetate), F-4 (1-deoxy-L-mannitol penta-acetate), G-5 (methyl 2-deoxy-D-*arabino*-hexonate tetra-acetate), G-7 and F-7 (2-deoxy-D-*arabino*-hexitol penta-acetate), F-9 (3-deoxy-D-*ribo*-hexitol penta-acetate), G-10 and F-10 (D-mannitol hexa-acetate), G-11 and F-11 (D-glucitol hexa-acetate), G-12 and F-12 (L-iditol hexa-acetate). In EI mass spectrometry, molecular ions of alditol acetates are not usually detected, but (M-OAc) and/or (M-CH_2OAc) ions are produced, together with fragment ions[3]. The fragmentation patterns are indicative of structure and allow comparison with authentic compounds. Thus, the identity of G-5 was confirmed as methyl 2-deoxy-D-*arabino*-hexonate; this compound is formed by reduction of 2-deoxy-D-*arabino*-hexono-1,4-lactone. Likewise, the 2-deoxyhexitol penta-acetate (G-7 and F-7) and 3-deoxyhexitol penta-acetate (G-8 and F-9) were identified. The intensity of the fragment ion, *m/e* 159, was strong (97%) for the 2-deoxy derivative and weak (28%) for the 3-deoxy analogue. The components of peaks F-4 to F-6 showed the same fragmentation patterns as 1-deoxy-L-mannitol penta-acetate, and the n.m.r. spectra (100 MHz, chloroform-*d*, internal tetramethylsilane) of the substances obtained by preparative g.l.c. showed the following signals for CMe: F-4 δ 1.22 (*d*, 3H, *J* 6.0 Hz); F-5, δ 1.26 (*d*, 3H, *J* 6.0 Hz); F-6, δ 1.26 (*d*, 3H, *J* 6.2 Hz). Peaks G- and F-10, 11, and 12 contained compounds each of which had a mass spectrum typical of a hexitol hexa-acetate, and they were identified (g.l.c.) as hexa-acetates

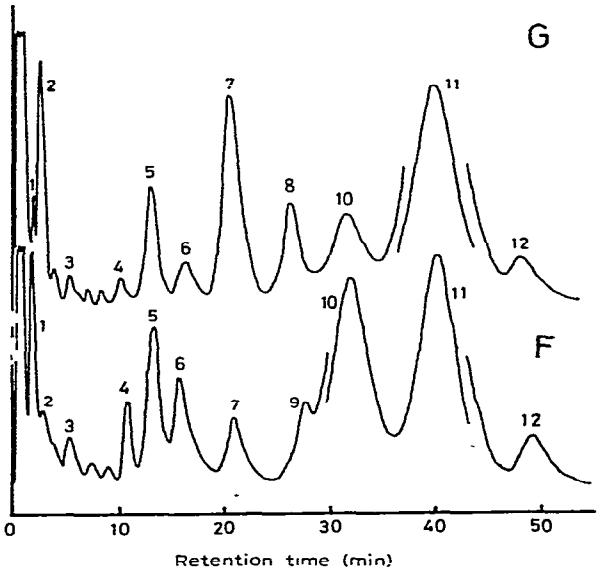

Fig.1. G.l.c. of the acetylated alditols prepared from irradiated solutions (20mM) of D-glucose (G) and D-fructose(F). Conditions: 8% DC QF-1 on Chromosorb W, stainless steel column (0.3 × 200 cm) at 200° injection temp. 280°, N_2 carrier gas (20 ml/min), flame-ionization detector.

of mannitol (10), glucitol (11), and iditol (12).

The deoxyhexitols are derived from deoxyhexosuloses and deoxyhexodiuloses, which may be produced by dehydration of the primary radicals of D-glucose and D-fructose, respectively, as in the formation of acetaldehyde from ethylene glycol[4] and deoxytetrose from erythritol[5]. To clarify the origin of the deoxyketo sugars, the irradiated solutions were freeze-dried, the residues were treated with aqueous sodium borodeuteride (C = O → CD.OD), and the products were acetylated and subjected to preparative g.l.c., followed by mass spectrometry. It was possible to show that the 2-deoxyhexitol was derived from 2-deoxy-D-*arabino*-1,4-hexonolactone and 2-deoxy-D-*erythro*-hexos-3-ulose for D-glucose, and from 2-deoxy-D-*threo*-hexos-5-ulose and/or 5-deoxy-L-*glycero*-2,4-hexodiulose for D-fructose; the 3-deoxyhexitol was derived from 3-deoxy-D-*erythro*-hexos-4-ulose and/or 4-deoxy-D-*erythro*-hexos-3-ulose for D-glucose, and from 4-deoxy-L-*glycero*-2,5-hexodiulose for D-fructose; and the 1-deoxyhexitol was derived from 1-deoxy-D-*threo*-2,5-hexodiulose for D-fructose.

The presence of mannitol suggests the formation of D-*arabino*-hexosulose (D-glucosone) by γ-radiolysis of D-glucose and D-fructose, although, for D-fructose, the majority of the mannitol would be derived from unreacted sugar. Iditol would be derived from 5-ulose by reduction, and its presence therefore suggests the formation of D-*xylo*-hexos-5-ulose and D-*threo*-2,5-hexodiulose from D-glucose and D-fructose, respectively.

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