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5,6-*O*-Isopropylidene-D-glucofuranose

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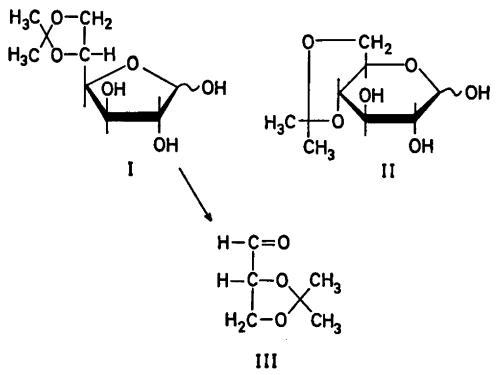
Treatment of D-galactose with acetone containing 15 – 20 % *N*,*N*-dimethylformamide and anhydrous cupric sulfate at reflux temperature, was found in a previous work [1] to give among other products 5,6-*O*-isopropylidene-D-galactofuranose in 16 % yield. A claim that the corresponding D-glucose derivative is formed by partial acid hydrolysis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose [2] is questionable, and the product obtained has later been suggested to be 1,2-*O*-isopropylidene-α-D-glucofuranose, based on the way of preparation and the given melting point.[3] An investigation of the possibility to prepare 5,6-*O*-isopropylidene-D-glucofuranose by treatment of D-glucose with anhydrous cupric sulfate in acetone-*N*,*N*-dimethylformamide was therefore undertaken, and is the subject of the present report.



Refluxing of D-glucose for 24 h with these reagents, led to the formation of several products, of which two exhibited chromatographic mobility indicating the presence of one *O*-isopropylidene group. These compounds were isolated by column chromatogtaphy on silica gel. The slowest moving compound was indistinguishable from 4,6-*O*-isopropylidene-D-glucopyranose (II)[3,4] whereas the fastest moving, obtained in 14 % yield, was identified as 5,6-*O*-isopropylidene-D-glucofuranose (I). The identification was based on the facts that oxidation with periodate gave 2,3-*O*-isopropylidene-D-glyceraldehyde (III), and the mass spectrum (Fig. 1a) was almost identical with that of 5,6-*O*-isopropylidene-D-galactofuranose [1] (Fig. 1b). A peak of high intensity in the mass spectrum at *m/e* 101 is strongly indicative of the

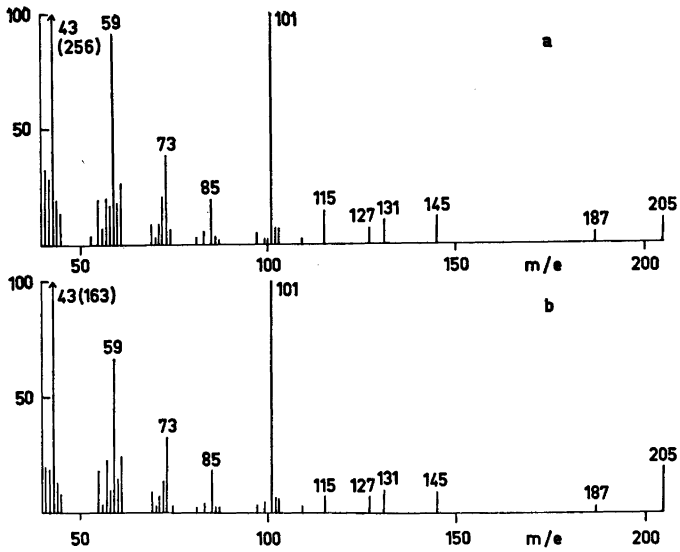


Fig. 1. Mass spectrum of (a) 5,6-*O*-isopropylidene-D-glucofuranose (I) and (b) 5,6-*O*-isopropylidene-D-galactofuranose.

presence of a 5,6-*O*-isopropylidene group,[5] the fragment results from cleavage of the C4 – C5 bond with the charge located at the C5 – C6 containing fragment. Other important peaks observed are those at *m/e* 205 ($M^+ - CH_3$), 187 (205 – H_2O), 145 (205 – AcOH), 127 (205 – H_2O – AcOH), 59 (Me_2COH^+), and 43 ($MeCO^+$), all of which are expected fragments of a mono-*O*-isopropylidene hexose.[5] The possibility of configurational isomerization of the parent hexose under the conditions employed in preparation of the mono-*O*-isopropylidene derivative is not likely, and it was shown that the 5,6-*O*-isopropylidene hexose (II) was a derivative of glucose by conversion to 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (IV).

The melting point of the obtained 5,6-*O*-isopropylidene-D-glucofuranose (I), 124 – 125 °C, is clearly different from that found for the compound formed by acid hydrolysis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose,[2] supporting the assumption [3] that the latter was the 1,2-*O*-isopropylidene derivative.

The present result is an additional example of the previously observed applicability of cupric sulfate-acetone, with or without *N*,*N*-dimethylformamide, in prepraration of otherwise inaccessible reducing mono-*O*-isopropylidene aldoses,[1,4,6] and also of the promoting effect of elevated temperatures on the formation of *O*-isopropylidene derivatives in furanose form.[1,5,7]

Experimental. Thin layer chromatography (TLC) was performed on Silica gel G in (A) benzene-ethanol 5:1 (v/v), (B) benzene-ethanol 3:1, and (C) chloroform-methanol 8:1. Paper electrophoresis was run in borate buffer, pH 10, on Whatman No. 1 paper. As spray reagent was applied diphenylamine-aniline-phosphoric acid.[8] Mass spectra were recorded on an AEI MS 902 mass spectrometer at an ionizing potential of 70 eV.

Reaction of D-*glucose with cupric sulfate-acetone-*N,N-*dimethylformamide.* D-Glucose (1 g) in *N*,*N*-dimethylformamide (30 ml) was poured into a stirred, refluxing mixture of acetone (125 ml) and anhydrous cupric sulfate (3 g). Stirring at reflux temperature was continued for 24 h. After cooling of the reaction mixture, benzene (100 ml) was added and the solution filtered, and subsequently stirred with solid sodium hydrogencarbonate for 30 min. The solution was filtered, concentrated to 3 ml under reduced pressure and then subjected to chromatography on a column (3 × 24 cm) of Silica gel H in solvent C. Three fractions were obtained; fraction 1 contained products with chromatographic mobilities indicating the presence of two *O*-isopropylidene groups, fraction 2 and fraction 3 contained mono-*O*-isopropylidene derivatives, both fractions were chromatographically homogeneous (TLC, solvents A and C).

*5,6-*O-*Isopropylidene-*D-*glucofuranose (I)* Evaporation of the solvent from fraction 2 gave a crystalline residue (171 mg, 14 %) which was recrystallized from ethyl acetate, m.p. 124 – 125 °C, $[\alpha]_D^{20}$ + 9° (c 2, water, 24 h). (Found: C 49.48; H 7.69. Calc. for $C_9H_{16}O_6$: C 49.09; H 7.27). The mass spectrum is shown in Fig. 1.

4,6-O-Isopropylidene-D-glucopyranose (II). Removal of the solvent from fraction 3 gave 4,6-*O*-isopropylidene-D-glucopyranose (II, 111 mg), it was recrystallized from ethyl acetate-acetone, m.p. 163–167 °C, $[\alpha]_D^{20}$ −5° (*c* 2, water, 48 h) (Lit.[3] m.p. 169.5–170.5 °C, $[\alpha]_D$ −7.3°). The product was chromatographically (TLC, solvents A and C) indistinguishable from authentic II.[4]

Periodate oxidation of 5,6-O-isopropylidene-D-glucofuranose (I). 5,6-*O*-Isopropylidene-D-glucofuranose (I, 40 mg) was dissolved in water (3 ml), and sodium periodate (200 mg) in water (3 ml) was added. Sodium hydrogencarbonate was added at intervals to neutralize the acid formed under the reaction. After 2 h, barium acetate (0.5 M) was added until the precipitation was complete, the precipitate was removed by centrifugation and the solvent concentrated under diminished pressure. The residue, still containing small amounts of water, was extracted by chloroform, the chloroform solution dried by sodium sulfate and the solvent was evaporated to give a chromatographically homogeneous syrup (11 mg), indistinguishable (TLC, solvent A) from 2,3-*O*-isopropylidene-D-glyceraldehyde (III),[9] the IR spectrum ($CHCl_3$) was identical with that of the authentic sample, stored a few days after preparation; both samples showed only a very weak carbonyl absorption at 1730 cm^{-1}, $[\alpha]_D$ +45° (*c* 0.5, benzene) (Lit.[9] +64.9°, *c* 5.75, benzene, freshly prepared III).

Hydrolysis of the oxidation product with 30 % aqueous acetic acid at 40 °C for 2 h and evaporation of the solvents gave a chromatographically (TLC, solvent B) and electrophoretically (M_{Glc} 0.75) homogeneous syrup, indistinguishable from authentic D-glyceraldehyde.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose (IV). 5,6-*O*-Isopropylidene-D-glucofuranose (I, 15 mg) was treated with acetone (2 ml) containing concentrated sulfuric acid (0.02 ml) for 2 h. The solution was neutralized with solid sodium hydrogencarbonate, filtered, and the solvent removed. The crystalline residue, indistinguishable from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (IV) by TLC (solvent A), was recrystallized from heptane-ethyl acetate, m.p. 106–109 °C (Lit.[10] 110–111 °C).

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