Two Septanose Diacetals of D-Glucose

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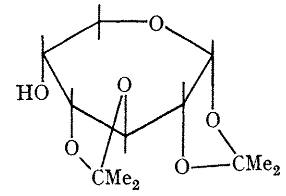
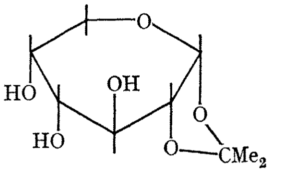
Summary Two novel di-*O*-isopropylidene derivatives of D-glucose in the septanose form have been isolated and characterized.

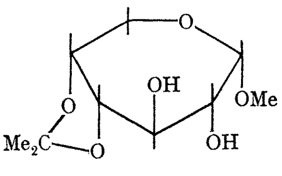
THE acid-catalysed condensation of D-glucose with acetone, long known[1] to produce 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose (I), as the major product, has now yielded (from a reaction of D-glucose with 4% sulphuric acid in acetone), besides the syrupy isomeric furanose derivative, 1,2 : 3,5-di-*O*-isopropylidene-α-D-glucofuranose (II) two novel acetals in which D-glucose has the seven-membered ring form. These have been identified as 1,2 : 3,4-di-*O*-isopropylidene-α-D-glucoseptanose (III) and 2,3 : 4,5-di-*O*-isopropylidene-D-glucoseptanose (IV). Compound (III), m.p. 146°, $[\alpha]_D$ $-61°$ ($CHCl_3$), has been isolated (in 1·9% yield) by chromatographing over silicic acid (using ether–light petroleum) the syrupy products remaining from crystallization of (I). Its structure has been determined by analysis of the n.m.r. spectra of (III) and its derived acetate and of the non-reducing product of selective acid hydrolysis of (III), 1,2-*O*-isopropylidene-α-D-glucoseptanose (V), m.p. 169°. In the n.m.r. spectrum of the triacetate of (V), the appearance of three 1-proton multiplets, shown to arise from three secondary hydrogen atoms on sequentially arranged carbon atoms, at low field, confirmed the suggested structure (III). Chemical evidence for the position of the free hydroxy-group in (III) was provided by preparation of the methyl ether of (III), followed by acid hydrolysis and identification of 5-*O*-methyl-D-glucofuranose as the anomeric tetrabenzoates.[2]



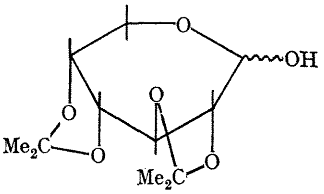
(III)



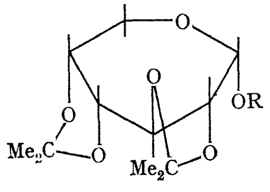
(V)



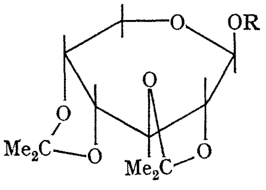
(X)



(IV)



(VI) R=Ac
(VIII) R=Me



(VII) R=Ac
(IX) R=Me

Mild acid hydrolysis (5% aqueous acetic acid at 20° for 5 days) of the syrupy products remaining from crystallization of (I) effected a reasonably selective hydrolysis of (I) and (II), leaving a mixture of (III) and (IV) together with other, as yet unidentified, products. Acetylation of this mixture yielded the easily crystallized acetate of (III), m.p. 151°, $[\alpha]_D$ −83·7° ($CHCl_3$), and chromatography of the remaining acetates over silicic acid (ether–light petroleum) afforded two acetates, identified as 1-*O*-acetyl-2,3 : 4,5-di-*O*-isopropylidene-α-D-glucoseptanose (VI), m.p. 115°, $[\alpha]_D$ +121° ($CHCl_3$), and 1-*O*-acetyl-2,3 : 4,5-di-*O*-isopropylidene-β-D-glucoseptanose (VIII), m.p. 100°, $[\alpha]_D$ −77·7° ($CHCl_3$), [corresponding to a 0·6% yield of (IV)]. Deacetylation of (VII) produced syrupy (IV) which gave rise to a mixture of (VI) and (VII) on re-acetylation.

Methylation of (IV) using MeI and silver oxide yielded two methyl ethers, methyl 2,3 : 4,5-di-*O*-isopropylidene-α-D-glucoseptanoside (VIII), m.p. 65°, $[\alpha]_D$ +137° ($CHCl_3$), and methyl 2,3 : 4,5-di-*O*-isopropylidene-β-D-glucoseptanoside (IX), m.p. 71°, $[\alpha]_D$ −112° ($CHCl_3$), separated by chromatography (silicic acid, ether–light petroleum). The arrangement of the two *O*-isopropylidene groups in (IV) was determined by selective hydrolysis of (VIII) (dioxan–0·1N-hydrochloric acid, 1 : 1, at 20° for 5 days). Two products were formed. One was identified as a mono-*O*-isopropylidene derivative, (X), and the other, (XI), was devoid of *O*-isopropylidene groups. The structures of (X) and (XI) followed from the n.m.r. spectra of their derived acetates. In the spectrum of the diacetate of (X), 1-H was found to be spin coupled to one of two mutually spin coupled protons resonating at lower field than 1-H. The two acetoxy-groups are therefore attached to C-2 and C-3. In the spectrum of the tetra-acetate of (XI), geminal hydrogen atoms 6-H and 6′-H ($J_{6,6'}$ 13·5 Hz.) came into resonance at much higher field than any of the other ring protons, establishing a septanose structure.

X-Ray crystallographic studies on a derivative of (III) and on two thioglycoside analogues of (VIII) and (IX) are in progress.

(*Received, July* 21*st*, 1969; *Com.* 1108.)

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[1] For a comprehensive review of cyclic acetals, see A. N. de Belder in "Advances in Carbohydrate Chemistry," ed. M. L. Wolfrom, Academic Press, New York, 1965, Vol. 20, p. 220.

[2] H. Kuzuhara and H. G. Fletcher, jun., *J. Org. Chem.*, **1967**, **32**, 2531.