Preliminary communications

2-Deoxy sugars

PART X. 5,6-O-CARBONYL-2-DEOXY-3-O-p-NITROBENZOYL-D-arabino-HEXOSYL BROMIDE. A STABLE, CRYSTALLINE O-ACYLGLYCOFURANOSYL HALIDE OF A 2-DEOXYHEXOSE*

The " α,β -methyl-2-deoxy-D-glucofuranoside" of Hughes *et al.*¹ has now been shown, by paper chromatographic analysis, to consist of an anomerically pure methyl 2-deoxy-D-*arabino*-hexofuranoside (II), plus substantial amounts of an approximately equal mixture of methyl α - and β -2-deoxy-D-*arabino*-hexopyranosides (III and IV), and unconsumed "2-deoxy-D-glucose" (2-deoxy-D-*arabino*-hexose, I). *p*-Nitrobenzoylation of the syrupy mixture arising from the methyl glycosidation of "2-deoxy-Dglucose" (I) led to a mixture of *p*-nitrobenzoic esters from which, by fractional recrystallization, there was obtained in pure form a methyl 2-deoxy-3,5,6-tri-*O-p*nitrobenzoyl-D-*arabino*-hexoside (V), m.p. 142–144° and also 168–169°; $[\alpha]_D^{24}$ –122.3° (*c* 1.00, chloroform). Calc. for C₂₈H₂₃N₃O₁₄: C, 53.72; H, 3.71; N, 6.72. Found; C, 53.70; H, 3.66; N, 6.49. Attempts to replace directly the severely hindered C-1 methoxyl group of V by hydrogen halide failed.

Methoxide-catalyzed saponification of V gave crystalline methyl 2-deoxy-parabino-hexofuranoside (II), m.p. $80-81^\circ$; $\left[\alpha\right]_{D}^{24} + 117.1^\circ$ (c 0.99, ethanol). Calc. for C7H14O5: C, 47.19; H, 7.92. Found: C, 47.20; H. 7.82. On conformational grounds and because of its strongly positive specific rotation, the α -D-anomeric configuration is provisionally assigned to II, as well as to V. Treatment of II with carbonyl chloride gave the 5,6-O-carbonyl derivative VI, m.p. 90–91°, $\left[\alpha\right]_{D}^{24}$ + 132.4° (c 1.00, ethanol). Calc. for C₈H₁₂O₆: C, 47.06; H, 5.92. Found: C, 47.21; H, 6.15. Nitrobenzoylation of VI gave methyl 5,6-O-carbonyl-2-deoxy-3-O-p-nitrobenzoyl-a-D-arabino-hexoside (VII), m.p. 213–214°; $[\alpha]_{\rm D}^{24} + 22.4^{\circ}$ (c 1.00, dichloromethane). Calc. for C15H15NO9: C, 51.00; H, 4.28; N, 3.96. Found: C, 51.08; H, 4.10; N, 3.96. Replacement of the C-1 methoxyl group of VII by hydrogen bromide in dichloromethane was facile, yielding crystalline 5,6-O-carbonyl-2-deoxy-3-O-p-nitrobenzoyl-Darabino-hexosyl bromide (VIII), m.p. $125-132^{\circ}$ (dec.); $[\alpha]_{D}^{24}$ -35.1° (c 0.436, acetone). The anomeric configuration of the bromide VIII has not yet been determined, but is presumed to be α -D, in which the bromine atom occupies a position trans to the substituted side-chain at C-4 of the furanose ring.

^{*}Presented before the Division of Carbohydrate Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Michigan, April 5, 1965. This work was supported in part by U.S. Public Health Service, Grant No. CA 07514, from the National Cancer Institute.

The bromide VIII reacted readily with silver *p*-nitrobenzoate to give 5,6-*O*-carbonyl-2-deoxy-1,3-di-*O*-*p*-nitrobenzoyl-D-*arabino*-hexose (IX), m.p. 204-205°; $[\alpha]_D^{24}$ -3.2° (*c* 0.286, dichloromethane). Calc. for C₂₁H₁₆N₂O₁₂: C, 51.64; H, 3.30; N, 5.74. Found: C, 51.82; H, 3.33; N, 5.65. The anomeric configuration of IX has



not yet been determined. The latter conversion indicated that the bromide VIII would have utility in the preparation of 2-deoxy-D-glucofuranosyl glycosides and 2-deoxy-D-glucofuranosyl nucleosides. As a test, we were successful in coupling VIII with 2,4-diethoxypyrimidine, by the Hilbert–Johnson procedure², to give 1-

Carbohydrate Res., 1 (1965) 93-95

(5,6-*O* carbonyl-2-deoxy-3-*O*-*p*-nitrobenzoyl-D-*arabino*-hexosyl)-4-ethoxy-2(1*H*)-pyrimidinone (X), m.p. 223–224.5°; $[\alpha]_{\rm D}^{24}$ -7.4° (*c* 1.54, dichloromethane). Calc. for C₂₀H₁₉N₃O₁₀:C, 52.07; H, 4.15; N, 9.11. Found: C, 52.21; H, 4.22; N, 9.09.

To the best of our knowledge, crystalline methyl glycofuranosides and crystalline *O*-acylglycofuranosyl halides of 2-deoxyhexoses were unknown prior to this work, full details of which will be published at a later date.

Department of Chemistry, Georgetown University, Washington, D.C. 20007 (U.S.A.) K.V. BHAT* W. WERNER ZORBACH**

REFERENCES

I I.W. HUGHES, W.G. OVEREND, AND M. STACEY, J. Chem. Soc., (1949) 2846. 2 G.E. HILBERT AND T.B. JOHNSON, J. Am. Chem. Soc., 52 (1930) 2001, 4489.

(Received February 23rd, 1965)

An unsaturated ketohexose

Although many unsaturated sugars have been prepared, the following is believed to be the first description of a simple unsaturated ketose.



An aqueous solution of 3-deoxy-2-O-methyl- β -D-erythro-hexofuranos-2-ene (I)¹ was treated with sodium borohydride at 30–40° to reduce the aldehydo form (Ia) present in solution. Sodium ions were removed from the mixosture by an ion-exchange resin, and the boric acid by distillation with methanol. The mild, acid treatment invol-

Carbohydrate Res., 1 (1965) 95-96

^{*}Post-doctoral Research Associate, Georgetown University, 1963–65. **To whom all enquiries regarding this paper should be addressed.