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GLUCOPYRANOSIDES OF 1-PROPANOL-2,3-DIHALIDES AND 2-PROPANOL-1,3-DIHALIDES

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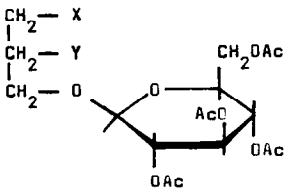
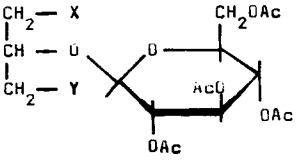
The preparation of a number of monoalkylglucopyranosides has been previously reported by Helferich (1) and Marquez et al.(2). This paper describes a convenient synthesis of several dihaloalkyl-glucopyranosides by two general procedures : The first method involves the reaction of dihalogeno-glycerol derivatives and the 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl-bromide. The reaction takes place when a solution of 2,3 or 1,3-dichloro or -dibromo-1-propanol or 2-propanol (0,03 mole) and 2,3,4,6-tetra-O-acetyl-α-D-glucopyrano-syl-bromide (0,02 mole), in anhydrous acetonitrile, with a mixture of mercuric bromide and mercuric cyanide (0,01 and 0,015 mole) is kept for 6-10 hr. at room temperature. The second method is based on replacing the chlorine or bromine atoms of the dihaloalkylgluco-pyranoside obtained in the first method by iodine atoms. The substitution is carried out by heating the halogenoglucoside with sodium iodide acetone solution.

By this procedure we have been able synthesise the β-glucopyranoside from 1-propanol-2,3-dihalide (I-IV) and 2-propanol-1,3-dihalide (V-VIII).



(I - IV)



(V - VIII)

Ac = $-\overset{O}{\overset{\|}{C}}-CH_3$

I, X=Cl, Y=Cl ; II, X=Br, Y=Br ; III, X=I, Y=Cl ; IV, X=I, Y=Br.

V, X=Cl, Y=Cl ; VI, X=Br, Y=Br ; VII, X=Cl,Y=I ; VIII,X=I,Y=I .

I.- 2,3-Dichloro-n-propyl-tetra-O-acetyl-β-D-glucopyranoside,m.p . 96-97° (methanol). $[\alpha]_D^{20}$ = -9,91 (chloroform, c=2,21). Yield, 50,2 %. II.- 2,3-Dibromo-n-propyl-tetra-O-acetyl-β-D-glucopyranoside,m.p. 94-96°.(methanol). $[\alpha]_D^{20}$ = -7,22 (chloroform, C=2,23). Yield, 55,9 % . III.-2,3-Iodochloro-n-propyl-tetra-O-acetyl-β-D-glucopyranoside . m.p.102-103°(methanol). $[\alpha]_D^{20}$=-10,0(chloroform,c=1,78).Yield,57,9 % . IV.- 2,3-Iodobromo-n-propyl-tetra-O-acetyl-β-D-glucopyranoside. m.p.91-93°(decomp)(methanol). $[\alpha]_D^{20}$ = -11,7 (chloroform, c = 1,8). Yield, 50,0 %. V.- 1,3-Dichloro-isopropyl-tetra-O-acetyl-β D-glupyranoside, m.p.125-126° (methanol). $[\alpha]_D^{20}$ = 16,2 (chloroform, c= 1,84). Yield, 55,6 %. VI.- 1,3-Dibromo-isopropyl-tetra-O-acetyl-β-D-glucopyranoside, m.p.127-128°(methanol). $[\alpha]_D^{20}$ = -19,5 (chloroform, c= 1,94).Yield,64,1 %. VII.- 1,3-Chloroiodo-isopropyl-tetra-O-acetyl-β-D-glucopyranoside,m.p. 118-119,5°(methanol). $[\alpha]_D^{20}$ = -20,5 (chloroform, c=1,84). Yield, 55,5 %. VIII.-1,3-Biiodo-isopropyl-tetra-O-acetyl-β-D-glucopyranoside,m.p. 133-134,5° (ethanol). $[\alpha]_D^{20}$ = -5,6 (chloroform, c=2,14). Yield, 75,2 %.

The elemental quantitative analyses are in agreement with these formulas.

We have not been able to carry out in the 2,3-dihalohydrin-β-glucoside derivatives the exchange of the two chlorine or bromine atoms by iodine atoms, which is probably due,to the steric hindrance,because of the proximity of the two halogens. However, in the 1,3-dihalohydrin-β-glucoside derivatives the replacement of both halogens atoms,for the bromo-glucoside, VI, occurs easily. On the other hand, the 1,3-dichloro-glucoside, V, replaces only a chlorine atoms, to give the iodochloro-glucoside, VII. At present we are performing some experiments looking for an exact explanation to these facts.

Deacetylation of the formed dihaloalkylglucosides by treatment with sodium metthoxide in methanol or barium hydroxide solution at room temperature,has not this far led to crystalline products. Wowever the residual sirups are easily reacetylated with acetic anhydride in pyridine at room temperature, yielding the initial acetylated glucosides.

In our laboratory, investigations of the reaction of these glucosides and other monohalogenoalkylglucosides with different substances, such as aromatic amines, pyridines and phenols,are now in progress

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