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THE DIRECT SYNTHESIS OF PSEUDOALDOBIURONIC ACID

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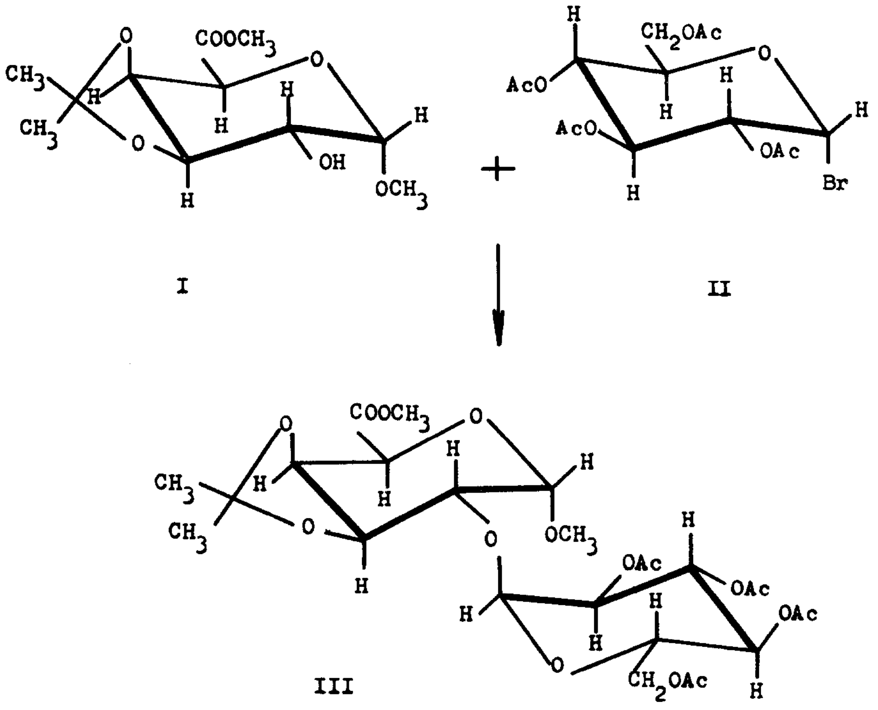
Recently the papers on the synthesis of pseudoaldobiuronic acids have appeared. 4-O-(β -D-glucopyranosyl)-D-glucuronic acid has been prepared by Lindberg and et al. (1) from cellobiose. In the course of several steps they suitably blocked all hydroxyl groups except the primary hydroxyl group of the reducing unit. The oxidation of this primary hydroxyl group and subsequent hydrolysis yielded pseudoaldobiuronic acid with the β -linkage. In the similar way was prepared its isomer with the α -linkage 4-O-(α -D-glucopyranosyl)-D-glucuronic acid by Hirasaka and Matsunaga (2), starting from maltose.

In both cases, the over-all yields were low-about 10 %, resp. 5 %.

We have successfully attempted the direct synthesis of pseudoaldobiuronic acid by means of modified Koenigs-Knorr method. We used mercuric cyanide as catalyst, which is known to conduct the formation of an α -linkage under specific conditions (3). The mixture of 200 mg of methyl(methyl-3,4-O--isopropyliden- α -D-galactopyranoside)uronate I and 750 mg of 2,3,4,6-tetra--O-acetyl- α -D-glucopyranosyl bromide ($\sim$ 1,5 molar excess) was shaken 21 days in $CHCl_3$ with 510 mg of $Hg(CN)_2$ ($\sim$ 1,5 molar excess).

The chromatographic separation on silica gel column (solvent benzene: acetone 8:2 v/v) yielded 17 mg of methyl/methyl 3,4-O-isopropyliden-2-O(2,3, 4,6-tetra-O-acetyl- α -D-glucopyranosyl)- α -D-galactropyranoside/uronate III, light yellowish sirup. The compound III gave on TLC chromatography on Silicagel G only one spot $R_F \doteq 0.42$ (benzene:methanol 95:5), well distinguished both from compound I ($R_F \doteq 0.18$) and compound II ($R_F \doteq 0.75$).



I

II

III

The infrared spectrum Fig.1 showed clearly strong peak at 1760 cm^{-1}, which can be attributed to the combination of the acetyl and the methyl ester groups and additionally strong double peak at 1380 cm^{-1}, attributed to the isopropylidene group. Also the NMR spectrum Fig.2 proved the presence of 1 isopropyliden, 4 acetyl, 1 methyl glycosidic and 1 methyl ester groups.

The optical rotation of compound III was estimated according to Hudson's rules to fall into the range of +130 - +150°. The measurement showed us the value $/\alpha/^{25}_{D}$ +149° (1.11; $CHCl_3$). The compound III on hydrolysis with water and Dowex 50 W (H^+ form) for 20 hours at 105 °C, followed by TLC (Silicagel G, benzen:acetic acid:methanol 2:2:6), yielded spots corresponding to D-glucose, D-galacturonic acid and methyl(methyl-α-D-galactopyranoside) uronate. Therefore we concluded that the prepared compound III is pseudoaldobiuronic acids with 1 → 2 α-linkage.

There is continued in the work, also in the attempt to prepare other pseudoaldobiuronic acids.

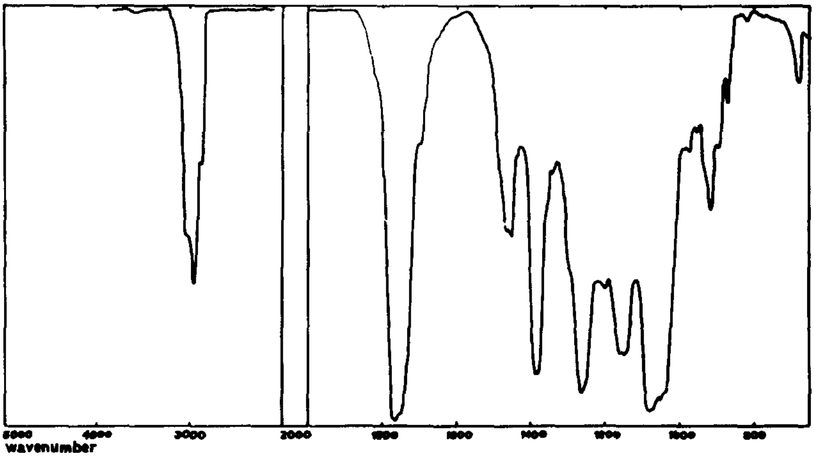


FIG.1. IR spectrum of the compound III (Unicam SP 200)

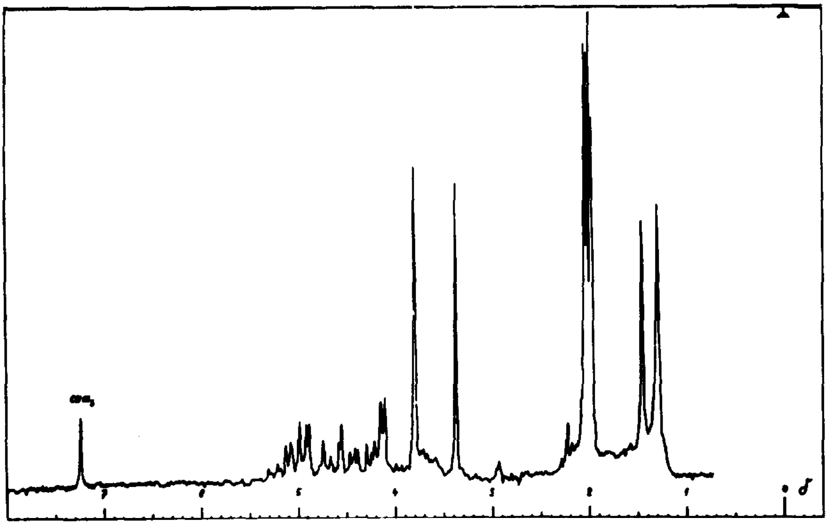


FIG.2 NMR spectrum of the compound III (Varian HA 100)

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