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**The Synthesis Of 1,6- Anhydro- 2, 3, 4- Tri-o- Benzyl-
β-D- Galactopyranose**

by

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The Synthesis Of 1,6- Anhydro- 2, 3, 4- Tri-o- Benzyl- β -D- Galactopyranose

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ABSTRACT

1,6- anhydro-2, 3, 4- tri -O- benzyl- β -D- galactopyranose was synthesized by benzylation of 1, 6- anhydro- β -D- galactopyranose triacetate as an oil. In order to synthesize them, β -D- galactopyranose pentaacetate and phenyl β -D-galactopyranoside tetraacetate have been obtained.

INTRODUCTION

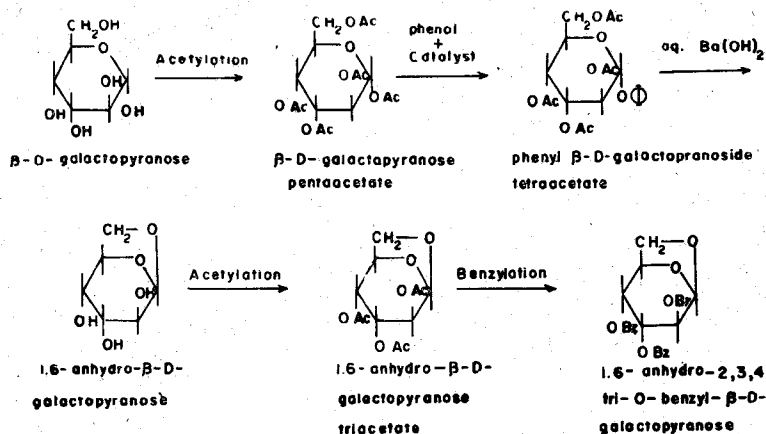
1,6- anhydro- β -D-galactopyranose triacetate and 1,6-anhydro- 2, 3, 4- tri-O-benzyl- β -D- galactopyranose are more important monomers to synthesize stereoregular 1 \rightarrow 6 β -D-galactopyranose polymers. 1,6- anhydro- β -D-galactopyranose was first synthesized by F. Micheel (1) from β -D- galactopyranosyl trimethyl ammonium bromide tetraacetate in presence of hot aqueous barium hydroxide. β -D-galactopyranose was pyrolyzed by F. Micheel (1) under high vacuum at 360C° and 1,6- anhydro- β -D-galactopyranose was isolated from its pyrolyzate . 1,6- anhydro- β -D-galactopyranose was recovered by C. S. Hudson and at. al. (2) jfrom the pyrolyzate of lactose, under the experimental conditions previously used for the preparation of 1,6-anhydro- β -D-mannopyranose from ivory nut.

In this work, β -D-galactopyranose was acetylated in the mixture of acetic anhydride and fused sodium acetate to W. Koenigs(3)

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This work has been done in Dept. of Forest Chemistry of State University College of Forestry at Syracuse University, Syracuse, N. Y.

and β -D-galactopyranose pentaacetate was obtained in a yield of 55 %. It was reacted with phenol in presence of p-toluenesulfonic acid to C. S. Hudson and at. al. (4) and phenyl β -D-galactopyranoside tetraacetate was prepared in a yield of 73 %. The last compound was degraded to 1,6-anhydro- β -D-galactopyranose in aqueous barium hydroxide solution to E. Fisher (5) It was acetylated in the mixture of acetic anhydride and pyridine according to I. A. Wolff (6) and 1,6-anhydro- β -D-galactopyranose triacetate was obtained in a yield of 22 %. 1,6-anhydro-2, 3, 4-tri-O-benzyl- β -D-galactopyranose was synthesized from 1,6-anhydro- β -D-galactopyranose triacetate to G. Zemple and at. al. (7) as an oil.



EXPERIMENTAL

Preparation of β -D-Galactopyranose Pentaacetate : 75 gr Fused sodium acetate (0, 914 mol) is mixed with 750 ml acetic anhydride (7, 955 mol) by heating on the steam bath. 150 gr D-Galactopyranose (0,833 mol) is added in above mixture. The reaction mixture is heated up on steam bath under reflux for 30 minutes. Then the unreacted acetic anhydride is stripped off on water bath under the vacuum. The residue is treated with 200 ml water and 250 ml chloroform. The mixture is neutralized with sodium-bicarbonate and decolorized with activated charcoal. The deco-

colorized filtrate is stripped off and, the residue is crystallized in absolute ethyl alcohol. M. P. 138-130 °C; $[\alpha]_D^{20} = + 29.07^\circ$ in chloroform; yield = 55 %. Reported: M. P. 142 C° (3), $[\alpha]_D^{20} = + 23C^\circ$ in chlooform (8)

Preparation of Phenyl β -D-Galactopyranoside Tetraacetate: 125 gr. β -D-galactopyranose pentaacetate (0,361 mol) is mixed with 118,6 gr phenol (1,261 mol) and 1,6 gr p-toluenesulfonic acid (0,008 mol). The mixture is heated up on the water bath at 98 C° by stirring under the vacuum of water aspirator. So, acetic acid formed during reaction is distilled off. The reaction is completed in about 90 minutes. The light brown residue is dissolved in 400 ml methylene chloride. The solution is neutralized with sodium hydroxide solution, washed out with water and, dried with anhydrous magnesium sulfate and, decolorized with activated charcoal. The clear solution is stripped off under vacuum on the water bath. The residue is recrystallized in absolute ethyl alcohol as white crystals. M. P. 122 C°, $[\alpha]_D^{20} = - 19.50^\circ$ in benzene, $[\alpha]_D^{20} = + 6,07^\circ$ in chloroform, yield = 73 %. Reported: M. P. 123-124 C°, $[\alpha]_D^{17} = - 26.4^\circ$ in benzen, $[\alpha]_D^{20} = - 0.7^\circ$ in chloroform, yield = 26 % (9) and M. P. 119-126 C°, $[\alpha]_D^{20} = - 0.75^\circ$ in chloroform, yield = 54 % (10). The data indicates that it has enough purity to synthesize the other compounds.

Preparation of 1,6-Anhydro- β -D-Galactopyranose Triacetate: 98,5 gr phenyl β -D-galactopyranoside tetraacetate (0,232 mol) dried in vacuum oven at 60 C° is treated with the solution of 293 gr Ba (OH)₂ · 8H₂O (0,929 mol) in 400 ml water and, refluxed for eight hours. The hot solution is neutralized with CO₂ in presence of phenolphthalein. The precipitate is separated by centrifuge. The combined centrifugate is stripped off under the vacuum on water bath. The residue is extracted with cold absolute ethyl alcohol. The extract is stripped off. The crude 1,6-anhydro β -D-galactopyranose (32 gr) is dried in vacuum oven at 80 C° overnight. It is acetylated in the mixture of 150 ml pyridine and 100 ml acetic anhydride at room temperature and kept overnight. The acetylation mixture is stripped off uner the vacuum on water bath. The residue is dissolved in 250 ml methylene chloride, shaken

150 ml water, neutralized with sodiumbicarbonate. The methylene chloride extract is dried with anhydrous magnesium sulfate and, decolorized with activated charcoal. The filtrate is stripped off and residue (43,3 gr) is recrystallized in ethyl etherligroin mixture until the specific rotation of compound reaches to $-5,4^\circ$ in chloroform. M. P. $73-74^\circ\text{C}$, $[\alpha]_D^{20} = -5,4^\circ$ in chloroform. Reported: M. P. 74°C , $[\alpha]_D^{20} = -5,6^\circ$ in chloroform (11). 12,5 gr. 16-anhydro- β -D-galactopyranose triacetate has been obtained. Yield = 22 % . Its structure was proved by NMR.

Preparation of 1,6-Anhydro-2, 3, 4-Trio-O-Benzyl- β -D-Galactopyranose:

12,5 gr. 16-anhydro- β -D-galactopyranose triacetate (0.043 mol) is dissolved in 125 ml benzylchloride (1.47 mol) containing 50 ml benzene. 26.8 gr powdered potassium hydroxide (0,478 mol) is added in above mixture. A trap is attached between reflux condenser and reaction flask to run reaction inder dry condition. The reaction mixture is stirred mechanically. The round flask containing above mixture is heated on the oil bath at 140°C for five hours. In this period 6 ml water is collected in trap. The reaction mixture is filtered from glass filter and residue is washed out with benzene. The filtrate is evaporated under the vacuum on the oil bath at 140°C . All attempts for crystallization of oily residue have been failed. NMR spectra showed that oil is 1,6-anhydro-2, 3, 4-tri-O-benzyl- β -D-galactopyranose. The oily residue was subjected to steam distillation by out -side heating. The oil was distilled out by steam. $[\alpha]_D^{20} = -42,4^\circ$, NMR spectra proved its structure, thin layer chromatography (12) showed that it contains impurities. The distillation out of oil by steam could not be reproduced.

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ÖZET

1,6- Anhydro- 2, 3, 4-Tri-O-Benzyl- β -D-Galactopyranose , 1,6- anhydro- β -D-galactopyranose triacetate'in benzilasyonu suretiyle bir yağ halinde elde edildi. Aynı zamanda β -D-galactopyranose pentaacetate ve phenyl β -D-galactopyranose tetraacetate'in de sentezi yapıldı.

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