

Action of Strong Acids on Acetylated Glycosides

II. Synthesis of Tetraacetyl- α -tertiary Butylglucoside

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In a previous communication¹ it was reported that attempts to prepare tetraacetyl- α -tertiary butylglucoside had been started and that the β -compound yielded acetochloroglucose by action of titanium tetrachloride.

Tetraacetyl- β -tertiary butylglucoside was treated with boron trifluoride in absolute benzene at room temperature. From the reactivity series: Isopropyl > ethyl > methyl, it was evident that the reaction time necessary would be still shorter than for the isopropyl derivative, which needed 30 minutes. For that reason 10 minutes was chosen. When the mixture was worked up, however, an oil of $[\alpha]_D^{20} + 80^\circ$ was obtained, which refused to crystallize. The experimental conditions were varied but the result was always the same. The oil was analysed with respect to alkoxy, acetyl and hydroxyl groups. The analyses were consistent with a mixture of about 60 % tertiary butylglucoside and 40 % 2,3,4,6-tetraacetylglucose. The glucoside ought to be insoluble in water and soluble in ether. 2,3,4,6-Tetraacetylglucose is known to be rather soluble in water and only slightly soluble in ether. It should therefore be possible to concentrate the glucoside by partition between ether and water. Thus, with a synthetic mixture of tetraacetyl- α -isopropylglucoside and β -2,3,4,6-tetraacetylglucose 1:1, the glucoside was isolated in an almost pure state and a yield of 80 % by partition between ether + petrol ether and water. When the oil was worked up in the same way, a crystalline compound was isolated from

the ether phase. It was purified by recrystallization from methanol and petrol ether and analysis showed it to be tetraacetyl- α -tertiary butylglucoside. M. p. 69 -70° . $[\alpha]_D^{20} + 113^\circ$ *.

Table 1. Molecular rotations of some alkyl glucosides.

Tetraacetylglucoside	M	2A	2B
α -methyl	+ 47400	+ 54200	+ 40600
β -methyl	- 6800		
α -ethyl	+ 49700	+ 58200	+ 41200
β -ethyl	- 8500		
α -isopropyl ..	+ 55800	+ 65300	+ 46300
β -isopropyl ..	- 9500		
α -tert. butyl..	+ 45700	50400	+ 41000
β -tert. butyl..	- 4700		

This seems to be the first α -glucoside of a tertiary alcohol that has been prepared. It is of interest to notice its small molecular rotation. The Hudson 2A value increases in the series: Methyl > ethyl > isopropyl, but for tertiary butyl it is even smaller than for methyl. The 2B value varies in the same way, but here the differences are smaller.

Tetraacetyl- β -tertiary butylglucoside. Tetraacetyl- β -tertiary butylglucoside, previously prepared by Veibel², was prepared here by a modification of the method of Zemplén for alkyl cellobiosides³.

Acetobromoglucose (22 g) was dissolved in absolute benzene (100 ml). Tertiary butylalcohol (40 ml) and mercury acetate

* All melting points uncorrected. All specific rotations in chloroform, about 2 %.

(7.8 g) were added and the solution was boiled for 15 minutes on the steam bath. When cold the solution was washed with water, dried over calcium chloride and concentrated under reduced pressure. The residue was recrystallized from ethanol. Yield 6.2 g. M. p. 141—143°. After further recrystallizations from ethanol the m. p. was raised to 144—144°.5. $[\alpha]_D^{20}$ —11°.

Tetraacetyl- β -tertiary butylglucoside and titanium tetrachloride. Tetraacetyl- β -tertiary butylglucoside (2 g) was dissolved in absolute chloroform (20 ml) and titanium tetrachloride (1.3 g) in absolute chloroform (12 ml) was added. The clear, yellow solution soon grew turbid and both white and yellow particles appeared in the resulting precipitate. The solution was heated for 40 minutes on the steam bath. When cold it was shaken with ice water, the chloroform phase washed with water and dried over calcium chloride. The brown solution was filtered through a column of aluminium oxide (Brockmann). After filtration it was yellow. The chloroform was evaporated under reduced pressure and the residue dissolved in ethanol and diluted with water. Pale yellow crystals (0.4 g) precipitated. M. p. 72—73°. $[\alpha]_D^{20}$ + 165°. By recrystallization from ether-petrol ether the m. p. was raised to 74—75° and the specific rotation to + 166°. As the substance proved to contain chlorine and the data are consistent with those of acetochloroglucose, it must evidently be that substance.

Tetraacetyl- α -tertiary butylglucoside. Tetraacetyl- β -tertiary butylglucoside (3 g) was dissolved in absolute benzene (75 ml), saturated with boron trifluoride and allowed to stand at room temperature for 10 minutes. The solution was then neutralized with absolute pyridine (10 ml) and shaken with cold bicarbonate solution. The benzene solution was washed with water, dried over sodium sulfate and con-

Aromatic Keto- and Hydroxy-polyethers as Lignin Models. I

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According to modern views regarding the structure of lignin, this material is built up from simple building stones containing an aromatic nucleus with a three carbon atom side chain. This idea is supported by a multitude of experimental results *e. g.* the fact that lignin and several lignin derivatives give a comparatively

concentrated under reduced pressure. The residual oil was dissolved in ether (40 ml) and extracted with water (5 × 100 ml). After each extraction the ether volume was made up to 40 ml again. Now petrol ether was added (20 ml) and the extraction with water continued (5 × 100 ml). The ether phase was dried over sodium sulfate and concentrated under reduced pressure. The residual oil was dissolved in ethanol and poured into water. An oil separated which soon solidified to white crystals of m. p. 65—66°. Yield 1.1 g. After recrystallization, first from methanol and then from petrol ether, the substance was obtained in a pure state. M. p. 69—70°. $[\alpha]_D^{20}$ + 113°.

The acetyl content was determined according to Clark.

$C_{10}H_{16}O_6(OCCH_3)_4$ (404.2)
Calc. Acetyl 42.6 Found Acetyl 42.5

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