

PARTIAL HYDROLYSIS OF ACYL 1,6-ANHYDRO- β -D-GLUCOPYRANOSE

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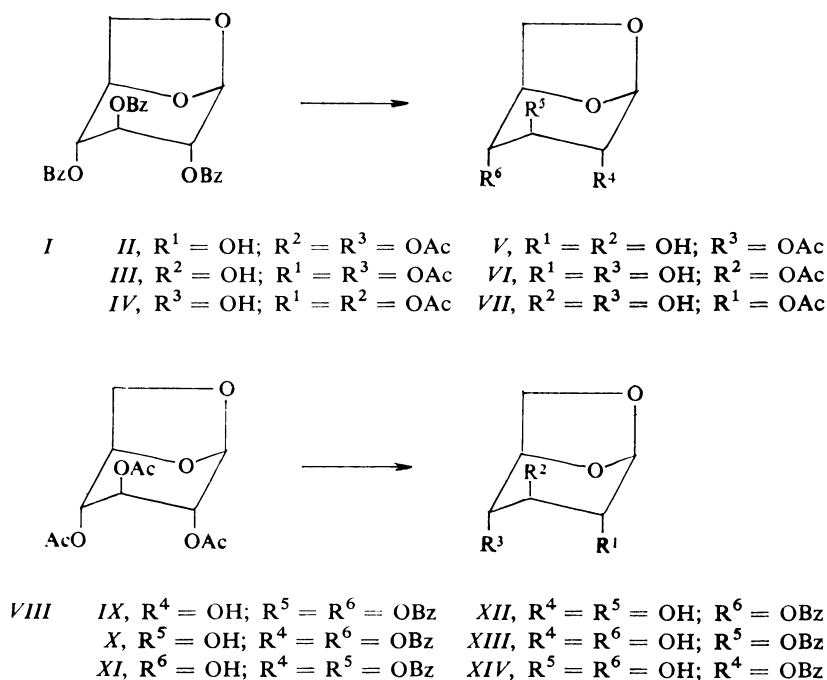
Received July 7th, 1983

Partial hydrolysis of per-O-acetyl- and per-O-benzoyl derivatives of 1,6-anhydro- β -D-glucopyranose with methanolic hydrogen chloride and hydrazine hydrate was investigated. The acyl group at C₍₃₎ is of substantial influence on the course of hydrolysis. The esterified hydroxyl group at C₍₃₎ was found to be most stable on acid hydrolysis with methanolic hydrogen chloride when compared with that at C₍₂₎, or C₍₄₎; on the other hand, this ester group is the most labile upon hydrolysis with hydrazine hydrate. Selectivity of the respective ester groups towards hydrolysis made it possible to prepare all variations of acetyl and benzoyl derivatives of 1,6-anhydro- β -D-glucopyranose.

Different reactivity of the respective hydroxyl groups of monosaccharides and their derivatives makes it possible to prepare saccharide derivatives with free hydroxyl groups in various positions. Partially esterified acyl derivatives of saccharides can be obtained by two different routes: by selective esterification of unsubstituted saccharides, as *e.g.* the preparation of 6-O-acetyl-D-glucopyranose¹⁻³, or by a partial deesterification of the fully esterified derivatives of saccharides. Reagents employed for hydrolysis are mostly of alkaline nature: NaOH solution⁴, hydroxylammonium acetate in pyridine⁵ and hydrazine. Fully acylated monosaccharides afforded with hydrazine acetate in dimethylformamide the corresponding 1-hydroxysugar derivatives⁶. Hydrazinolysis of fully acylated methylglycosides in pyridine or in pyridine-acetic acid yielded predominantly derivatives of glycosides with a C₍₂₎ hydroxyl group⁷.

Deacylations of fully esterified derivatives of saccharides in acid medium^{8,9} have sparingly been described, and the selectivity has not been investigated. This paper is pointed towards investigation of a partial deacylation of 1,6-anhydro-2,3,4-tri-O-acetyl- β -D-glucopyranose (*I*) (per-O-acetylated levoglucosan), or 1,6-anhydro-2,3,4-tri-O-benzoyl- β -D-glucopyranose (*VIII*) both in acid and alkaline media (Scheme 1). The course of deacetylation was monitored by gas chromatography; pure mono- and di-O-acyl derivatives were isolated by chromatography on silica gel. The position of O-acyl groups of new derivatives was determined by methylation analysis and by ¹³C NMR spectrometry. Thus *e.g.*, 1,6-anhydro-4-O-acetyl- β -D-

-glucopyranose (*V*) furnished 1,6-anhydro-2,3-di-O-methyl- β -D-glucopyranose¹⁰⁻¹⁷ by methylation with methyl iodide in the presence of Ag_2O followed by deacetylation with sodium methoxide. The position of O-acetyl groups in 1,6-anhydro-2-O-acetyl- β -D-glucopyranose (*VII*), 1,6-anhydro-3,4-di-O-benzoyl- β -D-glucopyranose (*IX*) and 1,6-anhydro-3-O-benzoyl- β -D-glucopyranose (*XIII*) was estimated similarly, by transformation to the corresponding known methyl derivatives¹⁷. Chemical shifts characterizing derivatives *V*, *VII*, *IX*, and *XIII* were ascribed respecting the substitution rules¹⁹ and according to comparison with the ^{13}C NMR spectral data of levoglucosan and its acyl derivatives.



SCHEME 1

Deacetylation of tri-O-acyl derivatives of 1,6-anhydro- β -D-glucopyranose can, at least in principal, afford a mixture of three di-O-acyl derivatives, three mono-O-acyl derivatives, and a fully deacylated product. Reactivity of acyl groups of various derivatives can considerably vary¹⁸ (tri-O-acyl-, di-O-acyl-, mono-O-acyl-). The presence of 1,6-anhydro ring markedly influences the reactivity of axial hydroxyl group at $\text{C}_{(3)}$. Another important point influencing the reactivity of acyl groups concerns reaction conditions of deacylation. As seen, the hydrolysis of 2,3,4-tri-O-acetyl derivative *I* in acid medium (Table I) afforded at the initial stage of hydro-

lysis (4 h), characterized by the presence of small amounts of mono-O-acyl derivatives, 2,3-di-O-acetyl derivative *IV* as a major product, less populated was the 3,4-di-O-acetyl derivative *II*, whilst the 2,4-di-O-acetyl derivative *III* was even less represented. Therefore, it can be concluded that in this stage of hydrolysis the stability of acetyl groups decreases as follows: acetyl group at $C_{(3)}$ > acetyl group at $C_{(2)}$ > acetyl group at $C_{(4)}$. Whereas in the first phase of deacetylation the ratio of the 2,3-di-O-acetyl derivative *IV* to 3,4-di-O-acetyl derivative *II* is roughly 2 : 1, this ratio undergoes change after 22 h and makes 1 : 2. This means that cleavage of one acetyl group from the molecule of tri-O-acetyl derivative *I* resulted probably in a change of reactivity of acetyl groups at $C_{(2)}$ and $C_{(4)}$; this statement can be backed by the fact that the acetyl group at $C_{(4)}$ in tri-O-acetyl derivative is more reactive, whilst the reactivity of di-O-acetyl derivatives is opposite. Investigation of the course of hydrolysis is complicated by occurrence of parallel side reactions involving migration of acetyl groups. The fact that during hydrolysis of 2,3-di-O-acetyl derivative *IV* (Table II) also the presence of 3,4-di-O-acetyl derivative *II* was evidenced indicated at least the possibility of migration of the acetyl group from $C_{(2)}$ to $C_{(4)}$.

The results of hydrolysis with methanolic hydrochloric acid made it possible to examine the influence of the reaction medium (Table I) and to compare them with those of hydrazine hydrate hydrolysis (Table III). The stable group upon acid hydrolysis was found to be that at $C_{(3)}$; upon alkaline hydrolysis this group is the most reactive. The course of hydrolysis with hydrazine hydrate was characterized by a nucleophilic attack of the lone electron pair of the nitrogen atom to the carbon atom of the protonized carbonyl. The acetyl group at $C_{(3)}$ was preferentially hydro-

TABLE I

Hydrolysis of 1,6-anhydro-2,3,4-tri-O-acetyl- β -D-glucopyranose in methanolic hydrogen chloride

Time h	Position of the acetyl groups ^a							
	$C_{(0)}$	$C_{(4)}$	$C_{(2)}$	$C_{(3)}$	$C_{(2,4)}$	$C_{(3,4)}$	$C_{(2,3)}$	$C_{(2,3,4)}$
2	0.0	0.7	0.5	2.3	1.6	7.7	12.6	74.4
4	0.4	1.6	1.2	5.6	2.3	13.0	26.4	49.6
6	1.4	3.7	2.4	11.6	2.7	16.0	27.0	35.1
8	2.8	5.1	3.4	24.1	2.6	20.0	22.8	19.1
16	13.9	8.0	4.7	41.8	0.05	12.9	12.9	5.7
22	23.0	7.4	3.9	48.4	1.1	9.4	5.0	1.9
24	29.2	6.8	3.3	49.3	0	8.9	1.8	0.7
48	64.1	1.5	0.6	33.9	0	0	0	0

^a Per cent of the particular acyl derivatives.

lyzed to furnish the 2,4-di-O-acetyl derivative *III*. Were the hydrolysis not discontinued by change of pH of the medium, a preferred hydrolysis of the acetyl group at C₍₂₎ would take place due to electron withdrawal by oxygen from the levoglucosan anhydride. This effect was even enhanced on hydrolysis of benzoylated derivatives of levoglucosan, which are by more stable when compared with acetylated derivatives. Upon alkaline hydrolysis of 1,6-anhydro-2,3,4-tri-O-benzoyl- β -D-glucopyranose (*VIII*) with hydrazine hydrate 4-O-benzoyl derivative *XII* was preferentially

TABLE II

Hydrolysis of 1,6-anhydro-2,3-di-O-acetyl- β -D-glucopyranose in methanolic hydrogen chloride

Time h	Position of the acetyl group ^a				
	C ₍₀₎	C ₍₂₎	C ₍₃₎	C _(3,4)	C _(2,3)
0.5	0.0	1.2	4.5	0.8	93.5
1	0.1	2.0	7.8	1.4	88.8
2	0.9	4.6	19.2	2.7	72.3
5	2.3	7.1	32.1	2.1	56.5
8	5.4	8.1	42.8	1.1	42.2
24	22.2	7.6	55.6	0.7	14.0
48	47.5	3.1	46.3	0	2.9

^a Percentage of the particular acyl derivatives.

TABLE III

Hydrolysis of 1,6-anhydro-2,3,4-tri-O-acetyl- β -D-glucopyranose in hydrazine hydrate

Time h	Position of the acetyl group ^a							
	C ₍₀₎	C ₍₄₎	C ₍₂₎	C ₍₃₎	C _(2,4)	C _(3,4)	C _(2,3)	C _(2,3,4)
0.5	0.0	0.5	trace	0.5	18.2	10.5	13.1	57.2
1	trace	2.7	1.1	1.7	26.2	15.0	15.4	38.0
2	0.1	4.5	1.9	3.0	33.6	13.7	16.8	26.3
4	0.2	7.8	3.2	5.8	36.7	15.7	16.7	13.8
7	0.4	11.2	4.9	8.9	38.7	14.3	15.5	6.1
24	0.9	15.2	6.4	14.6	36.7	13.4	11.9	0.9
36	1.2	16.5	7.2	15.6	38.0	11.3	9.9	0.4
48	1.2	15.6	7.1	15.4	40.4	10.3	9.9	0.2

^a Per cent of the particular acyl derivatives.

formed in an up to 50% yield. As found, the benzoylated derivatives of levoglucosan have, in comparison with the acetylated ones an enhanced resistance towards acid hydrolysis by methanolic hydrogen chloride. An acid hydrolysis of *I* with methanolic hydrogen chloride can lead to a total hydrolysis of all acetyl groups at a sufficiently long reaction time, the 1,6-anhydro ring being preserved; at the same reaction conditions, hydrolysis of *VIII* did not occur. This finding enabled us to synthesize a new 1,6-anhydro-3-O-benzoyl- β -D-glucopyranose *XIII* as follows: partial hydrolysis of *I* by hydrazine hydrate in alkaline medium afforded 2,4-di-O-acetyl derivative *III*, which, when esterified with benzoyl chloride, yielded 1,6-anhydro-2,4-di-O-acetyl-3-O-benzoyl- β -D-glucopyranose. The latter was hydrolyzed with methanolic hydrogen chloride to give derivative *XIII*. This procedure exemplifies how a suitable combination of various reactions (partial hydrolyses, preparations of mixed esters) and selection of reaction conditions of hydrolysis (acid or alkaline medium) can be useful for preparing esters of levoglucosan with free hydroxyl groups at any required position. These derivatives can, in turn, be a suitable starting material for further syntheses.

EXPERIMENTAL

Following starting material was used: 1,6-anhydro- β -D-glucopyranose¹³, m.p. 178–180°C, $[\alpha]_D = +67.2^\circ\text{C}$ (c 1, H₂O); 1,6-anhydro-2,3,4-tri-O-acetyl- β -D-glucopyranose¹⁴ (*I*), m.p. 109 to 110°C, $[\alpha]_D = -62.4$ (c 1, CHCl₃); 1,6-anhydro-2,3,4-tri-O-benzoyl- β -D-glucopyranose¹⁵ (*VIII*), m.p. 201–203°C, $[\alpha]_D = -36^\circ\text{C}$ (c 1, CHCl₃). Melting points were determined with a Kofler micro hot-stage, optical rotation was measured with a Perkin-Elmer, model 141, polarimeter. Chromatograph Hewlett-Packard, model 5830 A, equipped with a flame-ionizing detector was employed for gas chromatography. Stainless-steel, 30 cm long column, 2 mm i.d. was packed with 3% OV 225 over Supercorparate (grain size 0.135–0.150 mm). Heating of the column was programmed with a thermal gradient 1°C/min, starting temperature 135°C (6 min isotherm) to 220°C (30 min isotherm). The injection port temperature was 220°C, detector temperature 300°C; carrier gas nitrogen at a 15 ml/min flow rate. Results were computed in normalized percentage after calibration with reference substances.

The course of hydrolysis was monitored in acid medium of methanolic hydrogen chloride by gas chromatography of 0.1 ml samples withdrawn in certain time intervals; liberated hydroxyl groups were transformed into trifluoroacetyl derivatives by addition of 0.2 ml trifluoroacetic anhydride to the aliquot withdrawn. The same procedure was applied for monitoring the alkaline hydrolysis with hydrazine hydrate; the hydrolysis was stopped by addition of acetone. Trifluoroacetic anhydride (0.2 ml) was added to the residue of each sample from which the solvent was removed.

The ¹³C NMR spectra were recorded with a Jeol, model FX-60, spectrometer, at a 4 000 Hz spectral width, pulse width 3 μ s, 8 182 data points using noise decoupling and off resonance methods. Samples were dissolved in deuterium oxide and measured in 10 mm-cells at 20°C employing methanol as an internal reference whose chemical shift was 15.15 ppm downfield relative to tetramethylsilane.

Silufol sheets (Kavalier, Czechoslovakia) were used for qualitative chromatographic separation of acyl derivatives to monitor the hydrolysis; the spots were visualized by 5%-H₂SO₄ in me-

thanol and heating the sheet to 100°C. The product of hydrolysis was preparatively separated on silica gel-packed column (Silica gel L 100/250, Lachema, Czechoslovakia); solvent systems used were: A ethyl acetate–benzene–2-propanol (8 : 4 : 1), B benzene–ethyl acetate (7 : 3) and C benzene–ethyl acetate (2 : 1).

Hydrolysis of 1,6-Anhydro-2,3,4-tri-O-acetyl- β -D-glucopyranose (*I*) with Methanolic Hydrogen Chloride

Compound *I* (5 g) dissolved in methanol (45 ml) and 4%-hydrogen chloride in methanol (5 ml) was left to stand at room temperature; the hydrolysis was monitored either by thin-layer chromatography in system A (qualitative method), or by gas chromatography (quantitative method). Hydrolysis on preparative scale was stopped by neutralization with Amberlite IRA-402 in hydrogen-carbonate cycle. Results of hydrolysis are summarized in Table I.

Preparation of a mixture containing prevalently diacetyl derivatives of levoglucosan: The reaction mixture was neutralized after 8 h and concentrated under reduced pressure. The syrup was extracted with a mixture of water and chloroform (20 ml each). The aqueous layer dissolved almost all monoacetate, the chloroform one took diacetylated derivatives with a minute amount of monoacetates.

Chromatographic separation of levoglucosan diacetates: diacetates, remaining after evaporation of the solvent were chromatographed on a silica gel-packed column (4 × 90 cm) using solvent system A. In addition to mixed fractions, following pure portions were successively collected: the starting *I* (905 mg, 18%); 1,6-anhydro-2,4-di-O-acetyl- β -D-glucopyranose (*III*) 81 mg (2%) m.p. 129–132°C, $[\alpha]_D = -71^\circ\text{C}$ (*c* 0.5, CHCl_3), ref.¹²: m.p. 132–133°C, $[\alpha]_D = -70.2^\circ$; 1,6-anhydro-3,4-di-O-acetyl- β -D-glucopyranose (*II*) 820 mg (19%), m.p. 95–97°C, $[\alpha]_D = -80.1^\circ$ (*c* 1, CHCl_3), ref.¹²: m.p. 96–97°C, $[\alpha]_D = -79.5^\circ$; 1,6-anhydro-2,3-di-O-acetyl- β -D-glucopyranose (*IV*) 880 mg (21%), syrup, $[\alpha]_D = -43.2^\circ$ (*c* 1, CHCl_3), ref.¹²: $[\alpha]_D = -44.6^\circ$; 1,6-anhydro-3-O-acetyl- β -D-glucopyranose (*VI*) 795 mg (21%), m.p. 109–110°C, $[\alpha]_D = -61.8^\circ$ (*c* 1, H_2O), ref.¹⁶: m.p. 111–112.5°C, $[\alpha]_D = -62.2^\circ$.

Preparation of a mixture containing predominantly monoacetyl derivatives of levoglucosan: the reaction mixture was neutralized after 16 h only and evaporated at reduced pressure; water (10 ml) was added to the residue, and the solution was extracted with chloroform (4 ml). The aqueous layer containing monoacetates was evaporated *in vacuo* and the residue was separated by chromatography.

Chromatographic separation of levoglucosan monoacetates: The syrup obtained according to the preceding paragraph was separated by chromatography on a silica column (4.5 × 80 cm) in system A. In addition to the mixed fractions following ones were worked up to afford *VI*, 1.4 g (38%), m.p. 109–110°C, $[\alpha]_D = -61.5^\circ$ (*c* 1, H_2O); 1,6-anhydro-4-O-acetyl- β -D-glucopyranose (*V*), yield 262 mg (7%), m.p. 147–148°C, $[\alpha]_D = -62.5^\circ$ (*c* 1, H_2O); for $\text{C}_8\text{H}_{12}\text{O}_6$ (204.2) calculated: 47.06% C, 5.92% H; found: 47.28% C, 5.90% H. Position of the acetyl group was determined by methylation analysis: methylation of the sample with methyl iodide in the presence of Ag_2O followed by deacetylation led to 1,6-anhydro-2,3-di-O-methyl- β -D-glucopyranose, m.p. 43–45°C, $[\alpha]_D = -85.8^\circ$ (*c* 1, CHCl_3); these values are in line with those reported¹⁷. ¹³C NMR spectrum, δ (ppm): 102.46 for $\text{C}_{(1)}$, 71.29 for $\text{C}_{(2)}$, 70.77 for $\text{C}_{(3)}$, 74.02 for $\text{C}_{(4)}$, 75.06 for $\text{C}_{(5)}$, and 66.36 for $\text{C}_{(6)}$; α -effect 2.08, β -effect –2.86 for $\text{C}_{(3)}$, and –2.33 for $\text{C}_{(5)}$. Further were isolated: 1,6-anhydro-2-O-acetyl- β -D-glucopyranose (*VII*), yield 151 mg (4%), (4%), m.p. 159–161°C, $[\alpha]_D = -47.3^\circ$ (*c* 1, H_2O); for $\text{C}_8\text{H}_{12}\text{O}_6$ (204.2) calculated: 47.06% C, 5.92% H; found: 47.19% C, 5.91% H. Position of the acetyl group was determined by methyla-

tion analysis: after methylation with methyl iodide the product was deacetylated to obtain 1,6-anhydro-3,4-di-O-methyl- β -D-glucopyranose, syrup, $[\alpha]_D = -48.2^\circ$ (c 1, CHCl_3); ref.¹⁷: m.p. 41–43°C, $[\alpha]_D = -49.7^\circ$ (acetone). ^{13}C NMR spectrum, δ (ppm): 100.12 for $\text{C}_{(1)}$, 72.72 for $\text{C}_{(2)}$, 71.29 for $\text{C}_{(3)}$, 71.29 for $\text{C}_{(4)}$, 77.13 for $\text{C}_{(5)}$, and 66.23 for $\text{C}_{(6)}$; α -effect 1.04, β -effect -2.73 for $\text{C}_{(2)}$ and -2.98 for $\text{C}_{(4)}$. 1,6-Anhydro- β -D-glucopyranose, yield 0.4 g (13%), m.p. 178 to 180°C, $[\alpha]_D = -66.8^\circ$ (c 1, H_2O).

Preparation of VI: compound *I* (5 g) dissolved in methanol (45 ml) and methanolic hydrogen chloride (c. 4.4%, 5 ml) was allowed to stand at an ambient temperature for 24 h, neutralized with Amberlite IRA-402 in hydrocarbonate cycle, filtered and the filtrate was evaporated under diminished pressure to furnish a syrup, which, according to thin-layer chromatography, consisted of two major compounds: *VI* and 1,6-anhydro- β -D-glucopyranose in a 1 : 1 ratio. The syrup was dissolved in acetone (c. 50 ml) and left to crystallize for 24 h. Yield 0.5 g of *VI*, m.p. 110 to 111°C, $[\alpha]_D = -61.7^\circ$ (c 1, H_2O). Chromatographic separation of the mother liquor in solvent system A afforded additional 1.1 g of *VI*, total 1.6 g (42%).

Hydrolysis of *I* with Hydrazine Hydrate in Alkaline Medium

Hydrazine hydrate (c. 80%, 1 ml) was added to a solution of *I* (2.8 g) in pyridine (50 ml). The hydrolysis was stopped after a 7 h-standing at room temperature by addition of acetone (10 ml). The mixture was stirred for 2 h, evaporated and chromatographed on silica gel column (4×90 cm) with solvent system A to yield: *I* (200 mg, 7%); *III* (762 mg, 31%), m.p. 129–131°C, $[\alpha]_D = -71.4^\circ$ (c 1, CHCl_3); *II* (250 mg, 10%), m.p. 95–97°C, $[\alpha]_D = -79.5^\circ$ (c 1, CHCl_3); *IV* (257 mg, 10.5%), syrup, $[\alpha]_D = -42.6^\circ$ (c 1, CHCl_3); 1,6-anhydro-3-O-acetyl- β -D-glucopyranose (*VI*), 146 mg (7%), m.p. 109–110°C, $[\alpha]_D = -61.4^\circ$ (c 1, H_2O); *V* (185 mg, 9%), m.p. 146–148°C, $[\alpha]_D = -62.3^\circ$ (c 1, H_2O); *VII* (61 mg, 3%), m.p. 158–161°C, $[\alpha]_D = -47.1^\circ$ (c 0.5, H_2O).

Hydrolysis of 1,6-Anhydro-2,3,4-tri-O-benzoyl- β -D-glucopyranose (*VIII*)

Hydrazine hydrate (c. 80%, 4.9 ml) was added to a solution of *VIII* (4.74 g) in pyridine (80 ml). The mixture was allowed to stand at an ambient temperature for 4 h, then acetone (30 ml) was added and stirring was continued for additional 2 h. The product from which the solvent was evaporated was chromatographed on a silica gel column (4×90 cm) using solvent system B. Following products were obtained: the starting *VIII* (230 mg, 5%); 1,6-anhydro-3,4-di-O-benzoyl- β -D-glucopyranose (*IX*), 178 mg (4.9%), m.p. 36–38°C, $[\alpha]_D = -144.6^\circ$ (c 0.5, CHCl_3), for $\text{C}_{20}\text{H}_{18}\text{O}_7$ (370.3) calculated: 64.86% C, 4.89% H; found: 64.25% C, 4.86% H. Position of the benzoyl groups was determined by methylation analysis: methylation with methyl iodide followed by debenzoylation with sodium methoxide afforded 1,6-anhydro-2-O-methyl- β -D-glucopyranose, m.p. 92–94°C, $[\alpha]_D = -72.1^\circ$ (acetone); these data accorded with those reported¹⁷. ^{13}C NMR spectrum, δ (ppm): 103.17 for $\text{C}_{(1)}$, 69.91 for $\text{C}_{(2)}$, 73.68 for $\text{C}_{(3)}$, 72.64 for $\text{C}_{(4)}$, 74.98 for $\text{C}_{(5)}$, and 66.27 for $\text{C}_{(6)}$; α -effect: 0.70 for $\text{C}_{(4)}$ and 0.05 for $\text{C}_{(3)}$; β -effect: -1.38 for $\text{C}_{(2)}$ and -2.41 for $\text{C}_{(5)}$. Further were isolated: 1,6-anhydro-2,4-di-O-benzoyl- β -D-glucopyranose (*X*), yield 725 mg (20%), m.p. 128–130°C, $[\alpha]_D = -32.8^\circ$ (c 1, CHCl_3); ref.¹³: m.p. 128–129°C, $[\alpha]_D = -34^\circ$; 1,6-anhydro-2,3-di-O-benzoyl- β -D-glucopyranose (*XI*), 196 mg (5%), m.p. 135–137°C, $[\alpha]_D = +70.9^\circ$ (c 1, CHCl_3); ref.¹⁷: m.p. 137–138°C, $[\alpha]_D = +73^\circ$; 1,6-anhydro-3-O-benzoyl- β -D-glucopyranose (*XIII*), 110 mg (4%), m.p. 97–100°C, $[\alpha]_D = -58.6^\circ$ (c 0.5, methanol); for $\text{C}_{13}\text{H}_{14}\text{O}_6$ (266.2) calculated: 58.64% C, 5.30% H; found 58.64% C, 5.35% H. The position of benzoyl group was determined by methylation analysis in a usual way to give 1,6-anhydro-2,4-di-O-methyl- β -D-glucopyranose, syrup of $[\alpha]_D = -62.9^\circ$ (c 1, acetone) in agreement with¹⁷.

^{13}C NMR spectrum, δ (ppm): 102.65 for $\text{C}_{(1)}$, 69.39 for $\text{C}_{(2)}$, 75.24 for $\text{C}_{(3)}$, 69.39 for $\text{C}_{(4)}$, 77.31 for $\text{C}_{(5)}$, and 65.88 for $\text{C}_{(6)}$; α -effect: 1.61, β -effect: -2.55 for $\text{C}_{(4)}$ and 1.9 for $\text{C}_{(2)}$. Further were successively eluted: 1,6-anhydro-4-O-benzoyl- β -D-glucopyranose (*XII*), 1.3 g (49%), m.p. 124–126°C, $[\alpha]_{\text{D}} = -84.7^\circ$ (c 1, methanol), ref.¹¹: m.p. 123–126°C, $[\alpha]_{\text{D}} = -85^\circ$ (methanol); 1,6-anhydro-2-O-benzoyl- β -D-glucopyranose (*XIV*), 120 mg (4.5%), m.p. 162–163°C, $[\alpha]_{\text{D}} = +26.9^\circ$ (c 0.05, methanol), ref.¹¹ m.p. 162–164°C, $[\alpha]_{\text{D}} = +28^\circ$ (methanol); levoglucosan, 87 mg (5%), m.p. 178–180°C, $[\alpha]_{\text{D}} = 67.2^\circ$ (c 0.5, H_2O).

1,6-Anhydro-3-O-benzoyl- β -D-glucopyranose (*XIII*)

To 1,6-anhydro-2,4-di-O-acetyl- β -D-glucopyranose (*III*, 0.9 g) dissolved in pyridine (4 ml) benzoyl chloride (1.5 ml) was added with stirring at a temperature not exceeding 20°C. The mixture was after a 1 h-standing poured into ice-cold water (30 ml) and the oily product, which separated, was twice decanted with cold water (2×10 ml), dissolved in chloroform, dried with Na_2SO_4 and the solvent was evaporated *in vacuo*. Yield 1.24 g (95%) of syrupy 1,6-anhydro-2,4-di-O-acetyl-3-O-benzoyl- β -D-glucopyranose; this was in turn dissolved in methanol (12 ml) and hydrolyzed with methanolic hydrogen chloride (c. 4%, 1.2 ml) at an ambient temperature for 72 h. The solution was neutralized with Amberlite IRA-402 in a hydrocarbonate cycle and the solvent was removed under reduced pressure. The syrupy residue was crystallized from ethyl acetate; the yield of the title product was 805 mg (83%), m.p. 97–100°C, $[\alpha]_{\text{D}} = -58.8^\circ$ (c 1, methanol).

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Translated by Z. Votický.