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STUDIES ON OLIGOSACCHARIDES. XI*. 6- AND 6′-*O*-TRITYLMALTOSE PERACETATES†

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ABSTRACT

6′-*O*-Trityl-α-maltose heptaacetate (**1**) was prepared by detritylation of 6,6′-di-*O*-trityl-α-maltose hexaacetate (**5**) with 80% acetic acid at 100°, followed by retritylation with an equimolar ratio of reagent, and subsequent acetylation. When **5** was prepared by tritylation of maltose with a 3-molar equivalent of reagent followed by acetylation, the β-D anomer (**6**), of **5** was also isolated. A mixture of the six possible 6- and 6′-mono-, and 6,6′-di-*O*-tritylmaltose peracetates was obtained by direct tritylation of maltose with a 1:1 molar ratio of reagent and subsequent acetylation. All six products were isolated by chromatography on silica gel and by precise fractional crystallization; the yields of each were very different. The main product was 6′-*O*-trityl-β-maltose heptaacetate (**2**). The isomers having the trityl group on the nonreducing residue were much more dextrorotatory than those having the trityl group on the reducing residue. Studies on the molecular rotations suggested that changes in conformation at the glycosidic linkage, as expressed in torsional angles about the C–O and O–C bonds, may influence the magnitude of the optical rotations of these compounds. All of the six trityl derivatives gave positive, plain o.r.d. curves. An analog of 6′-*O*-trityl-α-maltose heptaacetate (**1**) having a trideuterioacetyl group at C-6, and an analog of 6-*O*-trityl-α-maltose heptaacetate (**3**) having a trideuterioacetyl group at C-6′, were synthesized to permit assignments of the 6-acetoxyl group signal in the n.m.r. spectrum of **1** and the 6′-acetoxyl group signal in the n.m.r. spectrum of **3**. The discrepancy in the chemical shifts of these acetyl methyl protons substantiated the foregoing postulates based on optical rotation.

INTRODUCTION

Two isomeric mono-*O*-tritylmaltose heptaacetates and one di-*O*-tritylmaltose hexaacetate have been synthesized from maltose by direct tritylation and subsequent

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acetylation[1]. The structures and the anomeric configurations of these two isomers were established as *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-tetra-*O*-acetyl-β-D-glucopyranose (**2**) and *O*-(tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranose (**3**), by n.m.r. spectroscopy and by the structural relationship between **3** and its β-D anomer (**4**); the latter had been prepared from maltosan by an authentic synthesis. The optical rotations of compounds **2**–**4** were not in accord with Hudson's Rules of Isorotation[2]; the specific rotation (+96° in chloroform) of the 6′-*O*-trityl β-D anomer **2** was about the same as that (+100° in chloroform) of the 6-*O*-trityl α-D anomer **3**, and much higher than that (+36° in chloroform) of the 6-*O*-trityl β-D anomer **4**. These anomalies are evidently caused by conformational differences.

Interest in these unusual optical rotations led to the present investigation, aimed at determining the specific rotations of all of the three anomeric pairs of the 6 and 6′-mono- and 6,6′-di-*O*-tritylmaltose peracetates. Studies on the n.m.r. spectra of these derivatives were also undertaken.

RESULTS AND DISCUSSION

A synthesis of the remaining monotrityl isomer, namely, *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-tetra-*O*-acetyl-α-D-glucopyranose (**1**) was required. As the direct tritylation of maltose with a 1:1 molar ratio of chlorotriphenylmethane, followed by acetylation, gave mainly the β-D anomer (**2**) and only a little of the desired α-D anomer (**1**), 6,6′-di-*O*-trityl-α-maltose hexaacetate (**5**) (prepared by tritylation of maltose in pyridine with 3 molar equivalents of the reagent and by subsequent acetylation) was detritylated at 100° with 80% acetic acid, retritylated with a 1-molar equivalent of the reagent, and then finally acetylated. Separation of the reaction mixture by chromatography on a column of silica gel afforded three crystalline products. One was the desired 6′-*O*-trityl-α-maltose heptaacetate (**1**), and the others were the 6-*O*-trityl isomer (**3**) and the 6,6′-di-*O*-trityl derivative (**5**). The specific rotation of **1** ($[\alpha]_D^{20}$ +131° in chloroform) was higher than that of the 6-*O*-trityl isomer **3** ($[\alpha]_D^{20}$ +88° in chloroform)*. The isomer having the trityl group on the nonreducing residue of maltose thus shows a much higher specific rotation than the one having the trityl group on the reducing residue.

Accompanying the 6,6′-di-*O*-trityl-α-maltose hexaacetate was a small proportion of the β-D anomer, which was isolated crystalline after chromatography on a column of silica gel and careful fractional crystallization. These anomers have almost the same R_F values by t.l.c., but their crystal forms are noticeably dissimilar. The α-D anomer, *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranose (**5**), crystallized as needles having m.p. 224.6–

*This value is not in agreement with that previously reported[1], but the difference between these values may arise from the different conditions used for measurement. The purity of the present preparation was established by elementary analysis and by t.l.c. on silica gel.

225.4°, $[\alpha]_D^{20}$ +98° in chloroform, and the β-D anomer, *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose (**6**) crystallized as plates having m.p. 126.4–126.8°, $[\alpha]_D^{20}$ +59° in chloroform. In the previous report[1], the anomeric configuration of the 6,6′-di-*O*-tritylmaltose hexaacetate obtained was not established, but it evidently was a mixture containing mainly the α-D anomer. 6,6′-Di-*O*-tritylmaltose hexaacetate has also been described by Josephson[3], and by Hirasaka, *et al.*[4], but they did not determine the anomeric configuration of their products. Josephson's compound had m.p. 116–119° and $[\alpha]_D^{22}$ +88°, and Hirasaka's product had m.p. 215–217° and $[\alpha]_D^{18}$ +88°. Probably neither of these products was a single compound.

As all of the six fully acetylated *O*-trityl derivatives of maltose were thus available and were characterized by chromatographic behavior, solubility, crystal form, m.p., and other data, simultaneous isolation of all of them, from a mixture of reaction products obtained by direct tritylation of maltose with a 1:1 molar ratio of reagent and subsequent acetylation, was attempted. The mixture of reaction products was carefully fractionated on a column of silica gel. Fractional crystallization of the fractions afforded four crystalline monotrityl derivatives and two crystalline ditrityl derivatives. The main product was 6′-*O*-trityl-β-maltose heptaacetate (**2**). Compound **4**, which appears to have the most sterically unfavored structure, was obtained in very low yield. Although the isolated yields of compounds **1** and **4** were low, their chromatographic similarity may have led to decreased yields.

The optical rotations of compounds **1**–**6** were measured under the same conditions and the molecular rotations ($[M]_D = [\alpha]_D \times$ mol. wt./100) were compared (Table I). Although polarimetry is a potential means for obtaining conformational information on optically active, organic molecules, the theoretical relationship

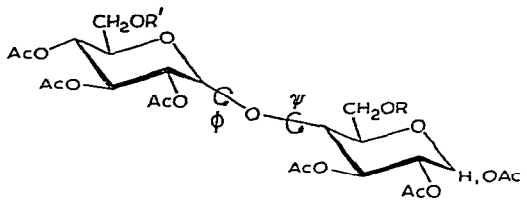
TABLE I

MOLECULAR ROTATIONS AND LINKAGE ROTATIONS (DEGREES)

Compound	$[M]_D$	$[M_{MeN}]+[M_R]$	$[A]$
1	1151	1041	+110
2	809	665	+144
3	774	1027	−253
4	325	715	−390
5	1057	1212	−155
6	637	896	−259
Octa-*O*-acetyl-α-maltose	833	856	−23
Octa-*O*-acetyl-β-maltose	425	480	−55

between optical rotation and molecular structure is not yet well understood, and attempted correlations of optical rotation and conformation have taken an empirical or semiempirical approach[5–10]. For the optical rotations of oligosaccharides, a

concept of linkage rotation [Λ] has been presented by Rees[11]. If the ring conformations of the two D-glucose residues in a maltose derivative maintain the ring conformations of the corresponding D-glucose derivatives, the molecular rotation of maltose derivative may be regarded as an algebraic summation of [M_{MeN}], (M_R], and [Λ], where [M_{MeN}] is the molecular rotation of the methyl α-glycoside of the non-reducing residue, [M_R] is the rotation of the reducing residue, and [Λ] is the linkage rotation. (More accurately, the [Λ] value should include a rotatory contribution arising from the presumed slight ring-distortion and change in the orientation of the $-CH_2OR$ group produced by interactions of substituents.) For this calculation, methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside[12] (**7**), methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside[13] (**8**), 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-D-glucopyranose (α-anomer[14] **9**, β-anomer[15] **10**) and penta-*O*-acetyl-D-glucopyranose (α-anomer[16] **11**, β-anomer[15] **12**) were synthesized and their optical rotations were measured under the same conditions. Their $[M]_D$ values (degrees) were as follows: **7**, 645; **8**, 460; **9**, 567; **10**, 255; **11**, 396; and **12**, 20. By using these $[M]_D$ values, the [Λ] values of the six *O*-tritylmaltose peracetates and a pair of maltose octaacetates were calculated (Table I). Considering the [Λ] values of the maltose octaacetates as a standard, it is



seen that introduction of an *O*-trityl group on the non-reducing residue causes an increase in [Λ]. On the other hand, tritylation of the reducing moiety renders the [Λ] value markedly negative. These data suggest that, in the molecule of the 6'-tritylated derivative, the dihedral angle ψ may change in such a way as to make a positive contribution to the linkage rotation, whereas, in the molecule of the 6-tritylated isomer, the dihedral angle ϕ may change in such a way as to make a negative contribution to the [Λ] value.

As a result, the relative orientation of the two D-glucose residues in the former molecule should differ from that in the latter molecule. Additionally, a change in the orientation of the $-CH_2OR$ group in the reducing residue might arise through interaction with the bulky substituent at C-4. The [Λ] value of the ditrityl ether is about the same as the sum of the [Λ] values for the 6- and 6'-monotrityl ethers. Perhaps the difference between the [Λ] value of the α-anomer and that of the corresponding β-anomer is due to a partial conformational change caused by interaction between the C-1 acetoxyl group and the C-6 substituent. When the C-6 substituent is an acetoxyl group, the difference is small, whereas the bulky trityl group at C-6 enlarges the discrepancy.

All six trityl derivatives gave positive, plain o.r.d. curves.

In the 60-MHz n.m.r. spectrum of each *O*-tritylmaltose peracetate in chloroform-*d*, signals arising from the methine and methylene protons lie between δ 3.0 and 6.4. This region can be subdivided into four non-overlapping regions; A (δ 3.0–3.5, 2H for monotrityl ethers and 4H for ditrityl ethers), B (δ 3.7–4.4, 4H for monotrityl ethers and 2H for ditrityl ethers), C (δ 4.6–5.5, 7H), and D (δ 5.7–6.4, 1H). Although assignment of all signals in regions A, B, and C could not be made at 60 MHz, the C-1 anomeric-proton signal in region D appeared as a well isolated doublet. The α-D anomers showed the H-1 resonances in the region δ 6.25–6.37, and those of β-D anomers were upfield in the region δ 5.74–5.78, in accord with the generalization[17] that axial protons usually resonate at higher field than equatorial protons in a similar chemical environment. The spin — spin coupling constants for the β-D anomers ($J_{1,2}$ 7.7–7.8 Hz) are about twice as large as those for the α-D anomers ($J_{1,2}$ 3.9–4.0 Hz), clearly indicating the configurations at C-1.

The signals of the acetyl methyl protons in the n.m.r. spectrum of octa-*O*-acetylmaltose are concentrated in the region δ 1.95–2.15, whereas the n.m.r. spectra of the 6′-*O*-tritylmaltose heptaacetates (**1** and **2**) show two signals shifted to higher field (δ 1.70 and 1.82) than the others. The spectra of the 6-*O*-tritylmaltose heptaacetates (**3** and **4**) show no signal in the same region, but the 6,6′-di-*O*-tritylmaltose hexaacetates (**5** and **6**) show one signal that is shifted upfield (δ 1.68 or 1.64). These n.m.r. data suggest that 6′-*O*-tritylmaltose heptaacetate has two acetoxyl groups that are shielded by the trityl group at C-6′, whereas the trityl group of 6-*O*-tritylmaltose heptaacetate exerts no specific effect on an individual acetoxyl group in the molecule. One of the two signals at higher field (δ 1.70) in the spectrum of 6′-*O*-tritylmaltose heptaacetate may be assigned to the AcO-4′ group, because the spectrum of 6,6′-di-*O*-tritylmaltose hexaacetate also shows an analogous signal, whereas the spectrum of 6-*O*-tritylmaltose heptaacetate shows no such signal. The other signal at higher field (δ 1.82) may be assigned to the 6-acetoxyl group. To prove this assignment, an analog of 6′-*O*-trityl-α-maltose heptaacetate (**1**) specifically deuterated in the 6-acetoxyl group was synthesized, essentially by the method (compare ref. 18) described for synthesis of 6′-*O*-trityl-α-maltose heptaacetate. 6,6′-Di-*O*-trityl-α-maltose hexaacetate was detritylated, retritylated with a 1-molar equivalent of the reagent, and deuterioacetylated with acetic anhydride-d_6 in pyridine. The spectrum of *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-*O*-trideuterioacetyl-α-D-glucopyranose (**1a**) was identical in all respects with that of **1**, except that one three-proton singlet (δ 1.82) in the spectrum of the latter was absent in that of the former, and this signal in the latter could thus be assigned unambiguously to the 6-acetoxyl group. An analog of 6-*O*-trityl-α-maltose heptaacetate (**3**) specifically deuterated in the 6′-acetoxyl group was also obtained as a by-product in the synthesis of **1a**. By comparing the spectrum of *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trideuterioacetyl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranose (**3a**) with that of **3**, it was established that the 6′-acetyl group of the latter resonated in the same spectral region (δ 1.98) as the other acetyl methyl protons.

This substantial difference between the chemical shifts of the acetyl methyl

protons in the spectra of 6-*O*-tritylmaltose heptaacetate and 6'-*O*-tritylmaltose heptaacetate accords with the speculation based on the optical rotation, but further studies by high-resolution n.m.r. spectroscopy are desirable, to furnish more-definitive evidence on the conformations.

EXPERIMENTAL

General. — Melting points were measured on a Yamato melting point apparatus MP-21 and are uncorrected. Evaporations were performed under diminished pressure. Optical rotations were determined with a Jasco DIP-SL automatic polarimeter. T.l.c. was performed with 0.25-mm layers of Silica Gel G (E. Merck, Darmstadt, Germany), activated at 130°, as the adsorbent and with benzene–ethyl acetate (7:2 v/v) as developer. Spots were detected by spraying with anthrone–sulfuric acid. Column chromatography was performed with Silica Gel No. II-B (Nakarai Chemical, Ltd.) as the adsorbent and components were eluted with the solvent specified. N.m.r. spectra were recorded with solutions in chloroform-*d* on a Varian A-60A (60 MHz) spectrometer, with tetramethylsilane as the internal standard.

Synthesis of O-(*2,3,4-tri*-O-*acetyl*-6-O-*trityl*-α-D-*glucopyranosyl*)-(*1→4*)-*tetra*-O-*acetyl*-α-D-*glucopyranose* (**1**). — 6,6'-Di-*O*-trityl-α-maltose hexaacetate (**5**, 10 g) was dissolved in 800 ml of 80% aqueous acetic acid and heated for 30 min at 100°. The solvent was evaporated off and traces of acetic acid were removed from the residue by repeated evaporation of ethanol from it. The residue was dissolved in methanol and cooled to 0°. Precipitated triphenylmethanol was filtered off and the filtrate was evaporated to a syrup, which was washed with petroleum ether and kept for 18 h in a vacuum desiccator to afford a white powder. The latter (7.1 g) was dissolved in 50 ml of dry pyridine, 3.1 g of chlorotriphenylmethane was added, and the solution was stirred for 64 h at 48–53°. A further 15 ml of freshly distilled, dry pyridine was added, the flask was cooled to 0°, and 20 ml of acetic anhydride was added. The stoppered flask was kept for 48 h at room temperature, and the solution was then poured into 1500 ml of ice and water, and stirred mechanically for 3 h. The precipitated solid was filtered off, washed with water, and dried under diminished pressure over phosphorous pentaoxide. The resultant solid was resolved on a column (5.5 × 62 cm) of silica gel by development with benzene–ethyl acetate (5:1 v/v). The effluent was examined by t.l.c. and the successive eluates containing material were combined into twelve fractions. Removal of solvent from these fractions led to syrups or crystals, which were purified by recrystallization from acetone–ethanol. 6'-*O*-Trityl-α-maltose heptaacetate (**1**) was obtained from fractions 5, 6 and 7, yield 0.94 g; m.p. 161.0–161.6°, $[\alpha]_D$ +131° (*c* 2, chloroform).

Anal. Calc. for $C_{45}H_{50}O_{18}$: C, 61.50; H, 5.73. Found: C, 61.41; H, 5.66.

As by-products, 6,6'-di-*O*-trityl-α-maltose hexaacetate (**5**) was also obtained (yield 0.48 g) from fraction 2, and 6-*O*-trityl-α-maltose heptaacetate (**3**) was obtained (yield 0.92 g) from fractions 9, 10 and 11, m.p. 191.8–192.0°, $[\alpha]_D$ +88° (*c* 2, chloroform).

Anal. Calc. for $C_{45}H_{50}O_{18}$: C, 61.50; H, 5.73. Found: C, 61.53; H, 5.91.

The first fraction contained only triphenylmethanol and the twelfth fraction contained mainly maltose octaacetate. Fraction 3, 4, and 8 were inseparable mixtures of the compounds in the preceding and succeeding fractions.

Isolation of the α- and β-anomers of 6,6′-di-O-tritylmaltose hexaacetate (**5** *and* **6**) — β-Maltose monohydrate (5 g, dried over phosphorus pentaoxide under diminished pressure) was dissolved in dry pyridine (100 ml) and the solvent was distilled at atmospheric pressure until the boiling point of the distillate attained 115°. The solution was brought to 80 ml with more dry pyridine, 12 g of chlorotriphenylmethane (3 molar equivalents) was added, and the stoppered flask was stirred for 40 h at 35–40°. The flask was then cooled to 0°, 20 ml of acetic anhydride was added, and the stoppered flask was kept for 25 h at room temperature. The solution was then poured into 3 l of ice and water, and stirred mechanically for 18 h. The precipitated solid was crystallized from acetone–ethanol. Repeating recrystallization from acetone–ethanol gave the pure α-anomer; yield 2.6 g, m.p. 224.6–225.4°, $[\alpha]_D^{20}$ +98.0° (*c* 2, chloroform).

Anal. Calc. for $C_{62}H_{62}O_{17}$: C, 69.00; H, 5.79. Found: C, 69.16; H, 5.64.

The mother liquids were collected and evaporated to a syrup, which was fractionated on a column (6.5 × 65 cm) of silica gel by using, successively, 2 l of benzene, and 3 l each of 10:1 (v/v) and 7:1 (v/v) benzene–ethyl acetate as developer. The effluent was examined by t.l.c., and the fractions containing dityrityl derivatives were combined into three fractions based on their contents of α- and β-anomers (1st, $\alpha < \beta$; 2nd, $\alpha = \beta$; and 3rd, $\alpha > \beta$). From all of these three fractions the α-anomer (**5**) crystallized first, as needles; yield 0.4 g. The β-anomer (**6**) crystallized as plates from the mother liquors after removal of the α-anomer; yield 1.3 g, m.p. 126.4–126.8°, $[\alpha]_D^{20}$ +59.0° (*c* 2, chloroform).

Anal. Calc. for $C_{62}H_{62}O_{17}$: C, 69.00; H, 5.79. Found: C, 68.94; H, 5.89.

Simultaneous isolation of the six O-tritylmaltose peracetates (**1**–**6**). — Dry β-maltose monohydrate (15 g) was tritylated with a 1:1 molar ratio of reagent and subsequently acetylated according to the procedure already described[1], to yield 37.0 g of a mixture. Ten g of the mixture was chromatographed on a column (6.5 × 85 cm) of silica gel by development with 27 l of benzene–ethyl acetate (7:1, v/v). The effluent was treated as already described, and the successive eluates containing *O*-tritylmaltose peracetates were combined into 21 fractions. Each fraction contained more than two components, but variations in the content of each component permitted to fractional crystallization of the six *O*-tritylmaltose derivatives from these fractions. The elution order was: polytritylated maltose peracetates (which were not examined), the 6,6′-di-*O*-trityl β-D anomer (**6**, R_F 0.64), its α-D anomer (**5**, R_F 0.62), the 6′-*O*-trityl β-D anomer (**2**, R_F 0.44), its α-D anomer (**1**, R_F 0.42), the 6-*O*-trityl β-D anomer (**4**, R_F 0.41), and its α-D anomer (**3**, R_F 0.38). The main product (**2**) crystallized from fractions 7–18, and then **5** was obtained from fractions 2–6 and also from the mother liquors of fractions 7–9, and **3** was crystallized from fractions 19–21. The minor components **1**, **4**, and **6** were obtained from the mother liquors of fractions 13, 18, and 23, respectively. The isolated derivatives were recrystallized

from acetone–ethanol: **1**, yield 0.2 g, n.m.r. δ 6.25 (doublet, $J_{1,2}$ 4.0 Hz); **2**, yield 5.1 g, m.p. 165.2–166.0°, n.m.r. δ 5.78 (doublet, $J_{1,2}$ 7.7 Hz); **3**, yield 0.4 g, n.m.r. δ 6.35 (doublet, $J_{1,2}$ 3.9 Hz); **4**, yield 0.03 g, m.p. 113.6–114.0°, n.m.r. δ 5.75 (doublet, $J_{1,2}$ 7.8 Hz); **5**, yield 1.2 g, n.m.r. δ 6.37 (doublet, $J_{1,2}$ 4.0 Hz); **6**, yield 0.8 g, n.m.r. δ 5.74 (doublet, $J_{1,2}$ 7.8 Hz).

O-(*2,3,4-Tri*-O-*acetyl*-*6*-O-*trityl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*1,2,3-tri*-O-*acetyl*-*6*-O-*trideuterioacetyl*-α-D-*glucopyranose* (**1a**). — Compound **1a** was synthesized from 6,6′-di-*O*-trityl-α-maltose hexaacetate (**5**, 5 g). The procedure was essentially the same as that described for the synthesis of **1** except that acetic anhydride-d_6 was used for acetylation. The mixture of reaction products was chromatographed on a column (4.5 × 59 cm) of silica gel with 5:1 (v/v) benzene–ethyl acetate as the developing solvent. The faster-running fractions contained 6,6′-di-*O*-trityl-α-D-maltose hexaacetate (**5**). The expected product (**1a**) was obtained from the middle fractions; yield 0.4 g, m.p. 160.6–161.0°, $[\alpha]_D^{17}$ +131.3° (*c* 0.48, chloroform). From the slow-running fractions an analog of **3**, *O*-(2,3,4-tri-*O*-acetyl-6-*O*-trideuterioacetyl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranose (**3a**) was also obtained; yield 0.8 g, m.p. 190.4–191.0°, $[\alpha]_D^{17}$ +87.0° (*c* 2.0, chloroform).

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