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Facile and regioselective preparation of partly O-benzylated D-glucopyranose acetates via acid-mediated simultaneous debenzylation–acetolysis

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Abstract—Fully O-benzylated methyl α-D-glucopyranoside shows a steady order in stepwise debenzylation when it is treated with sulfuric acid in acetic anhydride. Based on the order of debenzylation, regioselective preparations of 2,3,4-tri-, 2,3-, 2,4-, 3,4-di-, and 2-*O*-benzyl-D-glucopyranose acetates were facilitated in greater than 80% yields. The key points of the preparative reactions were the control of the acid strength and choice of suitable substrates.

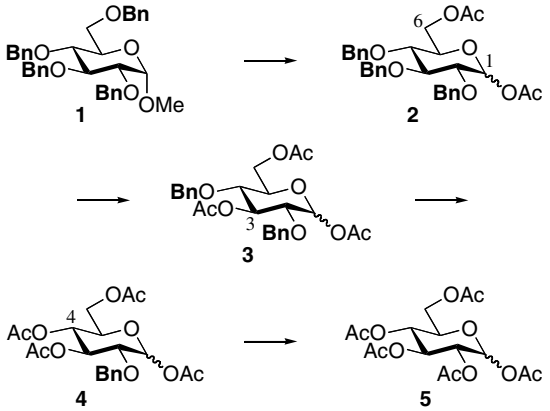
Keywords: Selective protection; Debenzylation; Acetolysis; Glucopyranose

1. Introduction

The benzyl group is one of the most useful protecting groups in synthetic organic chemistry. Its protecting ability has been verified in numerous syntheses, and a variety of methods for its installation and removal have been developed.[1] Benzyl-protected sugars are also significant for the syntheses of oligosaccharides and natural products.[2]

Although full benzylation of carbohydrate hydroxy groups is generally effortless,[3] regioselective partial benzylation requires ingenious strategies. For example, the following methods have been developed, which include the regioselective reductive ring-opening of the 4,6- or 1,2-*O*-benzylidene group,[4] metal complex (e.g., tin and copper) mediated benzylation,[5,6] and indirect methods that include the regioselective introduction of other protecting group(s), followed by benzyl protection of the remaining hydroxy group(s).[7] In addition, the regioselective debenzylation of fully benzylated sugars is an important part of the preparation of partly benzylated sugars.[8]

In our previous paper, we revealed that the benzyl groups of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**1**) were cleaved in the order of 6-*O*-Bn > 3-*O*-Bn > 4-*O*-Bn > 2-*O*-Bn under acid-mediated conditions (Scheme 1).[9] Thus, when **1** is acetolyzed in acetic anhydride containing 1% (v/v) sulfuric acid, the anomeric



Scheme 1. The debenzylation–acetolysis sequence of **1**.[9] Reagents and conditions: Ac_2O, 1% (v/v) H_2SO_4, rt.

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methyl, and 6-*O*-benzyl groups are first replaced by acetyl groups, and then the 3-, 4-, and 2-*O*-benzyl groups are also replaced in this order to afford the 2,3,4-tri-*O*-benzyl **2**, the 2,4-di-*O*-benzyl **3**, the 2-*O*-benzyl **4**, and then eventually the glucose pentaacetate **5**.

However, the reaction rate of this debenzylation is too fast to stop at any specific stage to obtain only one desired product. In our laboratory, mixtures were always produced and the separation process was troublesome, while products **2**, **3**, and **4** are the synthetically useful intermediates that have been used as building blocks for more complex compounds and natural products.[10] By controlling the reaction speed, therefore, this order of debenzylation should be applicable for the preparation of the partly benzylated sugars.

To control this stepwise reaction, we adjusted the strength of the used acid. We disclose here that the suitable choice of both substrates and the strength of the acid facilitated the synthesis of five kinds of partly benzylated D-glucopyranose acetates in greater than 80% yield.

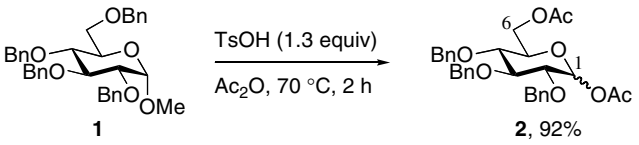
2. Results and discussion

First, we optimized the reaction conditions to produce **2** from **1** using *p*-toluenesulfonic acid (TsOH, Scheme 2), which is a weaker acid than sulfuric acid. When **1** was treated with TsOH in acetic anhydride, no distinct reaction occurred at room temperature in 5 h. However, at an elevated temperature, the anomeric methyl and the 6-*O*-benzyl groups began to be replaced to afford **2**. When the amount of TsOH was less than 1 equiv, the reaction was not completed within 15 h. On the other hand, the excessive use of the acid induced a further acetolysis. As a result, the suitable quantity of TsOH was found to be 1.3 equiv, and the reaction was completed in 2 h at 70 °C. Under these conditions, the isolated yield of **2** was 92%,[12] and thus the use of the proper amount of TsOH and choice of the appropriate reaction temperature would allow controlling such simultaneous debenzylation–acetolysis sequences. Similarly, the use of (1*S*)-camphor-10-sulfuric acid in acetic anhydride instead of TsOH also afforded **2** in 92% yield. However, we chose to use TsOH for our later investigation due to its lower cost.

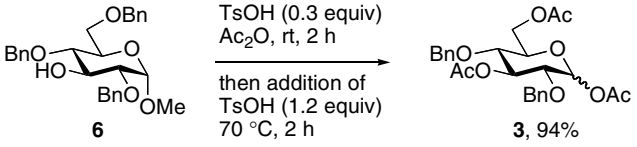
Next, the preparation of 2,4-di-*O*-benzyl **3** was carried out by the debenzylation–acetolysis sequence using TsOH. Although the sequence (Scheme 1) showed that dibenzylated **3** is a subsequent product of **2**, we could not determine optimum conditions that would produce **3** as the sole product starting from **1**. Therefore, we changed the starting material to **6** (Scheme 3), which can be prepared from methyl α-D-glucopyranoside, sodium hydride, and benzyl chloride without solvents (benzyl chloride assumes the role of the solvent) in 62% yield along with **1**.[11] Starting from **6**, the TsOH-mediated acetolysis conditions afforded **3** in 94% yield (Scheme 2).[8c] The reaction should start at room temperature with 0.3 equiv of TsOH to acetylate the free hydroxy group, then 1.2 equiv of TsOH was further added, and the reaction mixture was heated at 70 °C for 2 h to complete the replacement of the 6-*O*-benzyl group.

The suitable choice of substrates with control of the acid strength facilitated the preparation of other partly benzylated glucose derivatives, the 2,3-di-*O*-benzyl **7** and the 2-*O*-benzyl **4** (Scheme 4). Thus, starting from the 4,6-*O*-benzylidene substrate **8**,[12] **7** was prepared in 95% yield when 2 equiv of TsOH were used in acetic anhydride at 70 °C for 3 h. In addition, more vigorous reaction conditions afforded the 2-*O*-benzyl product **4** according to the order of debenzylation. Thus, the use of sulfuric acid instead of TsOH completed this selective debenzylation in 85% yield. Both reactions should be started at room temperature for first removing the *O*-benzylidene group.

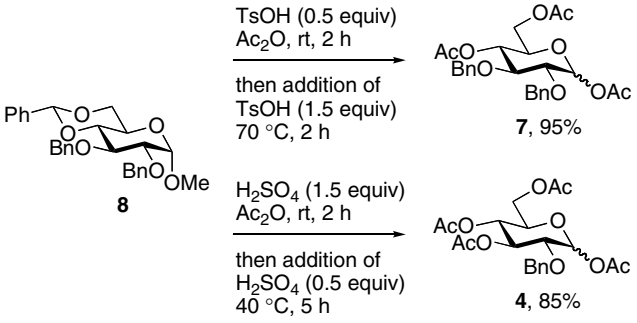
The selection of a 1,2-acetylidene compound **9** as the substrate facilitated the preparation of the 3,4-di-*O*-benzylated **10** (Scheme 5).[13] This protocol required three steps, but all operations could be completed in one



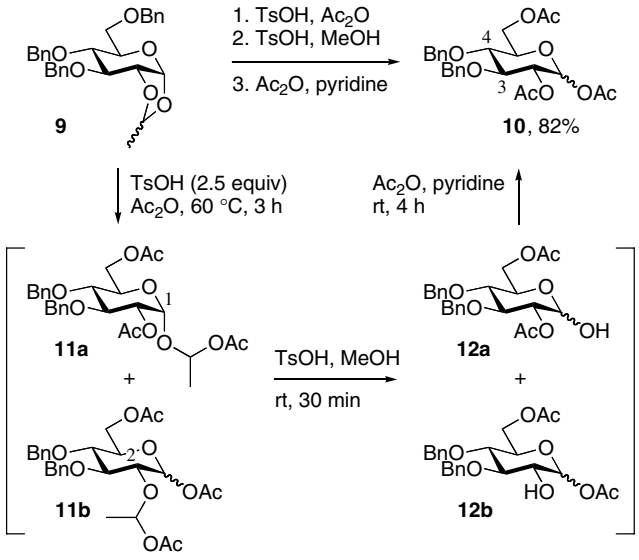
Scheme 2. Preparation of **2**.



Scheme 3. Preparation of **3**.



Scheme 4. Preparation of **7** and **4** from **8**.



Scheme 5. Preparation of **10** and its stepwise diagram.

pot. A stepwise description of the preparation is as follows. The acetolysis of **9** first produced both the 1- and 2-*O*-(1′-acetoxy)ethyl ethers **11a** and **11b**.[14] After removal of the acetic anhydride, the addition of methanol liberated the hydroxy groups at the 1- or 2-position to give a mixture of **12a** and **12b**. Then the removal of methanol, followed by the addition of acetic anhydride and pyridine, afforded **10** in 82% overall yield.

3. Conclusions

Control of the acid strength made the simultaneous debenzylation–acetolysis sequence (Scheme 1) possible for the practical preparation of partly benzylated D-glucose derivatives. The combination of the order of debenzylation and choice of suitable substrates facilitated the synthesis of five kinds of partly O-benzylated D-glucopyranose acetates, that are the 2,3,4-tri-, 2,3-, 2,4-, 3,4-di-, and 2-*O*-benzyl compounds, in greater than 80% yields. Because the reagents used for these transformations are very popular, and the procedures are simple, the debenzylation–acetolysis techniques should be a solution to preparing the partly benzylated derivatives of sugars that can be the building blocks, not only for more complex sugar compounds, but also for optically active natural products.

4. Experimental

4.1. General methods

The sulfuric acid solution in Ac_2O was prepared just prior to use. The reactions were checked by thin-layer chromatography (precoated Silica Gel 60, F-254). After each reaction was quenched, the reaction mixture was successively extracted twice with EtOAc, and washed with satd aq $NaHCO_3$ and brine, dried over $MgSO_4$, then concentrated under reduced pressure. The resulting residue was purified by column chromatography using Silica Gel 60 (70–230 mesh, 30 g) unless otherwise stated. The eluent for each chromatography is shown in each section. The α/β ratios of the products were determined by the integral of the H-1 peak in the ^1H NMR spectra, and part of the mixtures was separated by high-performance liquid chromatography (HPLC) for characterization. HPLC was performed using a normal phase column (4.6 × 250 mm) with detection by UV at 254 nm.

All new compounds were determined to be >95% pure by HPLC or ^1H NMR spectroscopy. The melting points are uncorrected. The infrared (IR) spectra are reported in wavenumbers (cm^{-1}). The high-resolution mass spectra (HRMS) were recorded using electrospray-ionization (ESI) and are reported in units of mass to charge. The nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ at 400 and 100 MHz for the ^1H and ^{13}C NMRs, respectively. The ^{13}C NMR chemical shifts are reported relative to the central line of the triplet for $CDCl_3$ at 77.0 ppm. For the notations regarding the NMR data, refer to the general methods and materials section in our previous report.[15]

4.2. 1,6-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-α- and β-D-glucopyranose (2)

To a solution of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**1**)[4] (390 mg, 0.717 mmol) in Ac_2O (4 mL) was added $TsOH{\cdot}H_2O$ (170 mg, 0.895 mmol), and the mixture was stirred for 2 h at 70 °C. The reaction mixture was then poured into ice water and subjected to the routine workup–purification sequence with 10:1 hexane–EtOAc as the eluent for chromatography to afford an anomeric mixture of **2** (347 mg, 92%, α:β = 1:0.3) as a colorless syrup. The NMR spectra of the compound were identical to those reported.[9,16]

4.3. 1,3,6-Tri-*O*-acetyl-2,4-di-*O*-benzyl-α- and β-D-glucopyranose (3)

To a solution of methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**6**)[11] (310 mg, 0.668 mmol) in Ac_2O (4 mL) was added $TsOH{\cdot}H_2O$ (38 mg, 0.20 mmol), and the mixture was stirred for 2 h at room temperature. Then $TsOH{\cdot}H_2O$ was further added (152 mg, 0.791 mmol), and the mixture was stirred for 2 h at 70 °C. The reaction mixture was then poured into ice water and subjected to the routine workup–purification sequence with 8:1 hexane–EtOAc as the eluent for chromatography to

afford an anomeric mixture of **3** (307 mg, 94%, α:β = 1:0.3) as a colorless syrup. The NMR spectra of the compound were identical to those reported.[9,17]

4.4. 1,4,6-Tri-*O*-acetyl-2,3-di-*O*-benzyl-α- and β-D-glucopyranose (7)

To a solution of methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**8**)[12] (268 mg, 0.580 mmol) in Ac_2O (4 mL) was added $TsOH{\cdot}H_2O$ (55 mg, 0.29 mmol), and the mixture was stirred for 2 h at room temperature. Then, $TsOH{\cdot}H_2O$ was further added (165 mg, 0.868 mmol), and the mixture was stirred for 2 h at 70 °C. The reaction mixture was then poured into ice water and subjected to the routine workup–purification sequence with 8:1 hexane–EtOAc as the eluent for chromatography to afford an anomeric mixture of **9** (269 mg, 95%, α:β = 1:0.3) as a colorless syrup. HPLC conditions: 6.5:1 hexane–EtOAc, 3.0 mL/min; t_R 14.6 min for the α isomer (**7a**), t_R 15.7 min for the β isomer (**7b**). The ^{1}H NMR spectra of **7a** were identical to those reported.[18] Data for **7b**: colorless syrup; $[\alpha]_D^{26}$ −3.3 (*c* 0.52, $CHCl_3$); IR (thin film) ν_{max} (cm^{-1}): 3032, 2920, 1748, 1454, 1368, 1222, 1055, 748, 700; ^{1}H NMR δ: 7.29–7.17 (m, 10H, Ar–H), 5.56 (d, $J_{H\text{-}1\text{–}H\text{-}2}$ 7.6 Hz, 1H, H-1), 5.00 (dd, $J_{H\text{-}3\text{–}H\text{-}4}$ 9.3 Hz, $J_{H\text{-}4\text{–}H\text{-}5}$ 9.5 Hz, 1H, H-4), 4.75 (d, *J* 11.5 Hz, 1H, Bn), 4.71 (*J* 11.2 Hz, 1H, Bn), 4.67 (*J* 11.2 Hz, 1H, Bn), 4.57 (d, *J* 11.5 Hz, 1H, Bn), 4.17 (dd, $J_{H\text{-}5\text{–}H\text{-}6a}$ 4.8 Hz, $J_{H\text{-}6a\text{–}H\text{-}6b}$ 12.4 Hz, 1H, H-6a), 3.98 (dd, $J_{H\text{-}5\text{–}H\text{-}6b}$ 2.4 Hz, $J_{H\text{-}6a\text{–}H\text{-}6b}$ 12.4 Hz, 1H, H-6b), 3.62 (dd, $J_{H\text{-}2\text{–}H\text{-}3}$ 9.0 Hz, $J_{H\text{-}3\text{–}H\text{-}4}$ 9.3 Hz, 1H, H-3), 3.60 (m, 1H, H-5), 3.57 (dd, $J_{H\text{-}1\text{–}H\text{-}2}$ 7.6 Hz, $J_{H\text{-}2\text{–}H\text{-}3}$ 9.0 Hz, 1H, H-2), 2.00 (s, 6H, Ac), 1.86 (s, 3H, Ac); ^{13}C NMR δ: 170.8 (s), 169.5 (s), 169.1 (s), 137.9 (s), 137.8 (s), 128.5 (d), 128.4 (d), 127.9 (d), 127.9 (d), 127.8 (d), 93.7 (d), 81.9 (d), 80.8 (d), 75.3 (t), 75.2 (t), 72.8 (d), 69.1 (d), 61.9 (t), 21.0 (q), 20.7 (q), 20.7 (q); HRESIMS (*m*/*z*) [M+Na^+]: calcd for $C_{26}H_{30}O_9$, 509.1788; found 509.1805.

4.5. 1,3,4,6-Tetra-*O*-acetyl-2-*O*-benzyl-α- and β-D-glucopyranose (4)

To a solution of **8**[12] (304 mg, 0.658 mmol) in Ac_2O (3 mL) was dropwise added 2% H_2SO_4 in Ac_2O (v/v) (2.65 mL, 1.0 mmol as H_2SO_4), and the mixture was stirred for 1 h at room temperature. Then further 2% H_2SO_4 solution was dropwise added (0.90 mL, 0.34 mmol as H_2SO_4), and the mixture was stirred for 5 h at 40 °C. The reaction mixture was then poured into ice water and subjected to the routine workup–purification sequence with 6:1 hexane–EtOAc as the eluent for chromatography to afford an anomeric mixture of **4** (244 mg, 85%, α:β = 1:0.25) as a colorless syrup. The NMR spectra of the compound were identical to those reported.[9,19]

4.6. 1,2,6-Tri-*O*-acetyl-3,4-di-*O*-benzyl-α- and β-D-glucopyranose (10)

To a solution of 3,4,6-tri-*O*-benzyl-1,2-*O*-ethylidene-α-D-glucopyranose (**9**)[13] (250 mg, 0.525 mmol) in Ac_2O (4 mL) was added $TsOH{\cdot}H_2O$ (250 mg, 1.31 mmol). The mixture was stirred for 3 h at 60 °C, and the Ac_2O was removed under vacuum. After cooling the residue in an ice-water bath, cold MeOH (15 mL) was added dropwise, and the solution was stirred at room temperature for 30 min. After evaporation of MeOH from the mixture, Ac_2O (1 mL) and pyridine (1.5 mL) were added. The mixture was stirred at room temperature for 4 h. Ac_2O and pyridine were then removed under vacuum, and 1 N HCl was added. The mixture was subjected to the routine workup–purification sequence with 8:1 hexane–EtOAc as the eluent for chromatography to afford an anomeric mixture of **10** (211 mg, 82%, α:β = 1:0.56) as a colorless syrup. HPLC conditions: 6.5:1 hexane–EtOAc, 3.0 mL/min, t_R 11.3 min for the α isomer (**10a**), t_R 12.8 min for the β isomer (**10b**). Data for **10a**: colorless syrup; $[\alpha]_D^{24}$ +79.7 (*c* 0.35, $CHCl_3$); IR (thin film) ν_{max} (cm^{-1}): 3032, 2922, 1747, 1454, 1369, 1238, 1051, 739, 700; ^{1}H NMR δ: 7.29–7.17 (m, 10H, Ar–H), 6.17 (d, $J_{H\text{-}1\text{–}H\text{-}2}$ 3.6 Hz, 1H, H-1), 4.97 (dd, $J_{H\text{-}1\text{–}H\text{-}2}$ 3.6 Hz, $J_{H\text{-}2\text{–}H\text{-}3}$ 10.0 Hz, 1H, H-2), 4.79 (d, *J* 10.7 Hz, 1H, Bn), 4.77 (d, *J* 11.2 Hz, 1H, Bn), 4.70 (d, *J* 11.2 Hz, 1H, Bn), 4.52 (d, *J* 10.7 Hz, 1H, Bn), 4.23 (dd, $J_{H\text{-}5\text{–}H\text{-}6a}$ 2.4 Hz, $J_{H\text{-}6a\text{–}H\text{-}6b}$ 12.0 Hz, 1H, H-6a), 4.18 (dd, $J_{H\text{-}5\text{–}H\text{-}6b}$ 3.6 Hz, $J_{H\text{-}6a\text{–}H\text{-}6b}$ 12.0 Hz, 1H, H-6b), 3.94 (dd, $J_{H\text{-}2\text{–}H\text{-}3}$ 10.0 Hz, $J_{H\text{-}3\text{–}H\text{-}4}$ 9.0 Hz, 1H, H-3), 3.89 (ddd, $J_{H\text{-}4\text{–}H\text{-}5}$ 10.0 Hz, $J_{H\text{-}5\text{–}H\text{-}6a}$ 2.4 Hz, $J_{H\text{-}5\text{–}H\text{-}6b}$ 3.6 Hz, 1H, H-5), 3.58 (dd, $J_{H\text{-}3\text{–}H\text{-}4}$ 9.0 Hz, $J_{H\text{-}4\text{–}H\text{-}5}$ 10.0 Hz, 1H, H-4), 2.05 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.90 (s, 3H, Ac); ^{13}C NMR δ: 170.6 (s), 169.9 (s), 168.9 (s), 138.1 (s), 137.3 (s), 128.6 (d), 128.5 (d), 128.2 (d), 128.1 (d), 127.8 (d), 127.5 (d), 89.6 (d), 79.9 (d), 76.6 (d), 75.5 (t), 75.3 (t), 71.7 (d), 71.3 (d), 62.3 (t), 20.9 (q), 20.8 (q), 20.6 (q); HRESIMS (*m*/*z*) [M+Na^+]: calcd for $C_{26}H_{30}O_9$, 509.1788; found, 509.1770. Data for **10b**: colorless syrup; $[\alpha]_D^{23}$ +30.0 (*c* 0.22, $CHCl_3$); IR (thin film) ν_{max} (cm^{-1}): 3032, 2916, 1757, 1454, 1367, 1232, 1059, 752, 700; ^{1}H NMR δ: 7.28–7.18 (m, 10H, Ar–H), 5.55 (d, $J_{H\text{-}1\text{–}H\text{-}2}$ 8.3 Hz, 1H, H-1), 5.03 (dd, $J_{H\text{-}1\text{–}H\text{-}2}$ 8.3 Hz, $J_{H\text{-}2\text{–}H\text{-}3}$ 9.0 Hz, 1H, H-2), 4.75 (d, *J* 11.0 Hz, 1H, Bn), 4.74 (d, *J* 11.5 Hz, 1H, Bn), 4.62 (d, *J* 11.5 Hz, 1H, Bn), 4.50 (d, *J* 11.0 Hz, 1H, Bn), 4.24 (d, $J_{H\text{-}6a\text{–}H\text{-}6b}$ 12.0 Hz, 1H, H-6a), 4.15 (dd, $J_{H\text{-}5\text{–}H\text{-}6b}$ 3.0 Hz, $J_{H\text{-}6a\text{–}H\text{-}6b}$ 12.0 Hz, 1H, H-6b), 3.67 (dd, $J_{H\text{-}2\text{–}H\text{-}3}$ 9.0 Hz, $J_{H\text{-}3\text{–}H\text{-}4}$ 9.0 Hz, 1H, H-3), 3.69–3.58 (m, 2H, H-4 and H-5), 2.01 (s, 3H, Ac), 1.96 (s, 3H, Ac), 1.87 (s, 3H, Ac); ^{13}C NMR δ: 170.6 (s), 169.4 (s), 169.2 (s), 137.7 (s), 137.2 (s), 128.5 (d), 128.5 (d), 128.1 (d), 128.1 (d), 127.9 (d), 127.8 (d), 91.9 (d), 82.8 (d), 76.9 (d), 75.3 (t), 75.0 (t), 73.8 (d), 71.9 (d), 62.4 (t), 20.8 (q), 20.8 (q), 20.7

(q); HRESIMS (m/z) [M+Na$^+$]: calcd for $C_{26}H_{30}O_9$, 509.1788; found, 509.1771.

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