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Note

Synthesis of novel ferrocene labelled steroidal derivatives via palladium-catalysed carbonylation. X-ray structure of 17-(*N*-(4′-((2-ferrocenyl-ethenyl)-carbonyl)-phenyl)carbamoyl)-5α-androst-16-ene ☆

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Abstract

Homogeneous catalytic carbonylation of some representative steroidal substrates (alkenyl iodides/enol triflates **1**–**5**) has been carried out in the presence of (*E*)-1-(4′-aminophenyl)-3-ferrocenyl-prop-2-en-1-one (**6**) as the nucleophile. The products **1a**–**4a** were obtained in moderate to good yield (43–75%) and were characterised with various spectroscopic methods (^{1}H-, ^{13}C NMR, IR, MS).

The solid state structure of 17-(*N*-(4′-((2-ferrocenyl-ethenyl)-carbonyl)-phenyl)-carbamoyl)-5α-androst-16-ene (**1a**) has also been determined by X-ray crystallography.

Keywords: Carbonylation; Ferrocene; Chalcone; Steroids; Palladium

1. Introduction

During the past few years electrochemical biosensors have attracted an increasing interest as an alternative for the analytical determination of biomolecules. Good stability and favourable electrochemical properties makes ferrocene derivatives good candidates for such purposes. Ferrocene-derived devices are used as anion and cation sensors [2], DNA biosensors [3] and as mediators of the electron transfer between active sites of oxidoreductases (e.g. glucose oxidase [4]) and electrodes. As a result, several methods have been reported for the synthesis of ferrocene-linked biomolecules, especially amino acids and peptides [5]. However, there are only a few examples for connecting ferrocene derivatives with the steroid skeleton [6]. Ethynylferrocene has effectively been coupled to cholesterol [7] and estradiol derivatives [8]. In the last example it was shown that despite the addition of the bulky metallocene unit, the compound was still well-recognised by an antibody specific to estradiol.

Other steroidal ferrocene derivatives (e.g. cholesteryl ester of ferrocenecarboxylic acid and ferrocenylmethyl cholestanyl ether) were shown to form vesicles depending on

☆ Study on ferrocenes, Part 20. Part 19: see Ref. [1].

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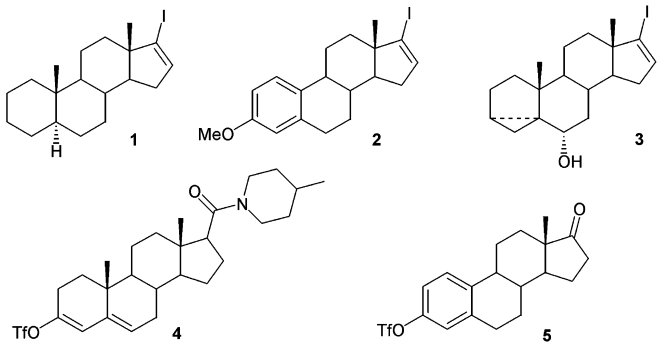


Fig. 1. Steroidal substrates used in the carbonylation reaction.

the oxidation state of iron in the metallocene unit and could serve as components of redox-switchable membranes [9].

Some steroids bearing the ferrocenyl moiety have advantageous pharmacological properties. (*N*-Ferrocenylmethyl)amines derived from vicinal steroidal amino alcohols and amines were found to exhibit outstanding antimicrobial activity against mycobacteria and multi-resistant staphylococci [10].

In this paper we report on the homogeneous catalytic carbonylation of some representative steroidal substrates (**1**–**5**, Fig. 1) in the presence of (*E*)-1-(4′-aminophenyl)-3-ferrocenyl-prop-2-en-1-one (**6**) as the nucleophile. This method represents a new route for connecting the ferrocene unit with the steroidal skeleton. The presence of the ferrocene moiety may allow electrochemical detection of the new compounds. Besides, as various ferrocenyl chalcone derivatives were shown to exhibit antimalarial [11], antibacterial [12], antiplasmodial [13] and antitumor activity [14], the connection of the steroid skeleton to such molecules may enhance biological activity as a result of increased lipophilicity of the products.

2. Results and discussion

2.1. Synthesis of ferrocene labelled steroidal derivatives (*1a*–*4a*)

Steroidal iodo-alkenes (17-iodo-androst-16-ene **1**, 17-iodo-3-methoxy-estra-1,3,5(10),16-tetraene **2**, 17-iodo-6α-hydroxy-3α,5α-cycloandrost-16-ene **3**, Fig. 1), an enol-triflate (3-triflyloxy-17β-(3′-methyl-pentan-1′,5′-diyl)-carboxamido-androsta-3,5-diene **4**) and an aryl triflate (3-triflyloxy-estra-1,3,5(10)-trien-17-one **5**) were reacted with (*E*)-1-(4′-aminophenyl)-3-ferrocenyl-prop-2-en-1-one (**6**) under atmospheric carbon monoxide in the presence of Et_3N as a base and an *in situ* generated palladium(0)-triphenylphosphine catalyst to afford products **1a**–**4a** (Scheme 1). The reactions were followed by TLC. Chalcone **6** has been prepared by base-catalysed Claisen–Schmidt condensation of ferrocenecarboxaldehyde with 4′-amino-acetophenone [15].

In the carbonylation reactions palladium(II) acetate was used as catalytic precursor. The formation of Pd(0) species from the generally used $Pd(OAc)_2$–PPh_3 system has previously been proved by cyclic voltammetry and ^{31}P NMR [16]. The reduction of Pd(II) to Pd(0) is due to PPh_3, which is itself oxidised to triphenylphosphine oxide.

In the palladium-catalysed carbonylation, 1,4-dioxane was found to be superior compared to DMF which is usually used as solvent in coupling reactions. In the case of dioxane, it is easier to achieve water-free conditions, which is essential for the completion of the desired reaction. In

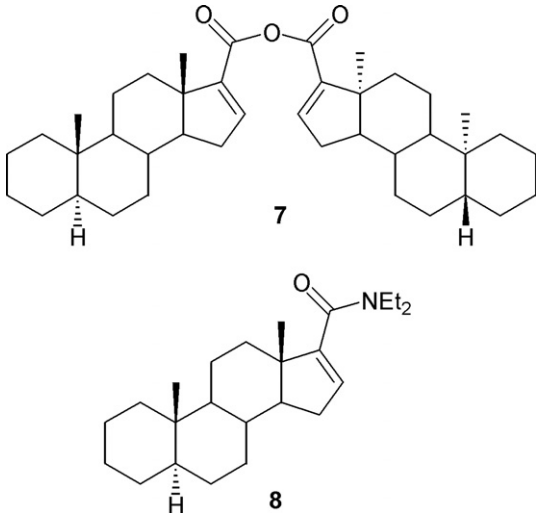
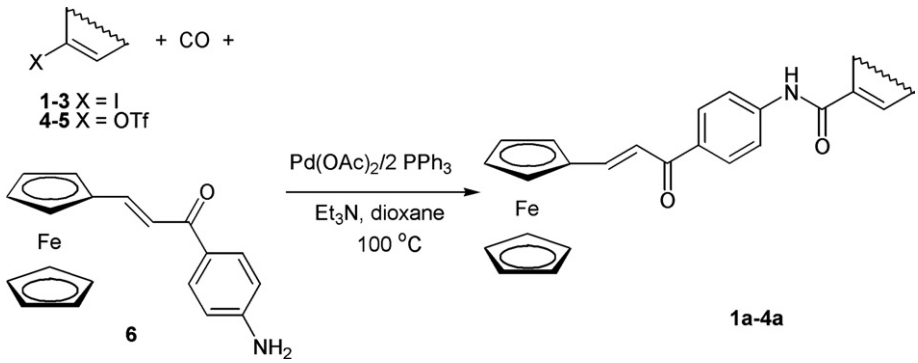


Fig. 2. Side products in the palladium-catalysed carbonylation of **1**.



Scheme 1. Palladium-catalysed carbonylation in the presence of chalcone **6** as the nucleophile.

Table 1
Ratio of isolated steroidal derivatives during aminocarbonylation of **1**[a]

Entry	Solvent	1/6	Yield of steroidal products[b] (%)			
			1a[c]	**7**	**8**	**1** (Recovered)
1	DMF	1/1	15 (15)	25	11	–
2	1,4-Dioxane	1/1	32 (32)	10	10	–
3	1,4-Dioxane	1/2	20 (10)	8	5	–
4	1,4-Dioxane	1.2/1	47 (56)	8	10	–
5	1,4-Dioxane	2/1	40 (80)	9	19	17

[a] Reaction conditions: 0.2–0.4 mmol **1**, 0.01 mmol $Pd(OAc)_2$, 0.02 mmol PPh_3, 0.2–0.4 mmol **6**, 100 μl Et_3N, 2 ml solvent, 1 bar CO, 100 °C, 16 h. Column chromatography (silica gel, eluent: toluene/ethanol = 50/3).
[b] mmol Steroid/mmol substrate **1**.
[c] In parentheses: yield of **1a** based on the amount of chalcone **6** (mmol **1a**/mmol **6**).

the presence of traces of water, the formation of steroidal 17-carboxylic acid anhydrides (e.g. **7**, Fig. 2) were also observed. Water, that is present as an impurity, successfully competes with the poor nucleophile chalcone **6** during carbonylation. In this case, the steroidal substrates are partly converted to carboxylic acid anhydrides via palladium-catalysed hydroxycarbonylation [17]. In 1,4-dioxane, the ratio of **7** could be decreased considerably (Table 1, entry 1 vs. entries 2–5) due to the lower water-content of the solvent.

Although aminocarbonylation of steroidal substrates is usually carried out in the presence of a high excess of the amine nucleophile, a great amount of unreacted chalcone **6** made separation of some of the products in appropriate purity (>99%) difficult (see below). At the same time, relatively low concentration of the poor nucleophile **6** (1–2 equiv relative to the steroidal substrates) led to the formation of *N*,*N*-diethyl-carboxamido derivatives (e.g. **8**, Fig. 2) as side products in less than 10% yields due to a competing reaction of Et_3N used as hydrogen halide scavenger. The C–N bond of tertiary amines were proved to be cleaved by palladium-complexes under carbonylation conditions in the presence of organic halides resulting in the formation of tertiary amides as products [18]. The formation of *N*,*N*-diethyl-carboxamido steroids as side products had been observed before by ourselves, during the synthesis of steroidal phenyl ketones via palladium-catalysed carbonylation of alkenyl iodides using $NaBPh_4$ as a phenyl source [19].

Optimal steroidal substrate/chalcone ratio was determined in aminocarbonylation of **1** (Table 1, entries 2–5). Product **1a** could be isolated only in 32% and 20% yields, using **1** and **6** in 1/1 and 1/2 ratios, respectively, although complete conversion of **1** to products **1a**, **7** and **8** was observed according to TLC (Table 1, entries 2 and 3). By the increase of the **1/6** ratio, the amount of unreacted chalcone **6** decreased which made separation of the product **1a** easier. At the same time, the amount of steroidal byproducts, especially **8**, and unreacted **1** increased (Table 1, entry 5). Optimal yields of products **1a**–**4a** (43–75%) were obtained by the use of 1.2 equiv of steroidal substrates relative to chalcone **6**.

Compound **5** was found to be completely unreactive under the conditions employed. No carbonylation products could be detected even using the bidentate ligand 1,3-bis(diphenylphosphano)propane (dppp) that had effectively been used before in the carbonylation of steroidal aryl triflates of poor reactivity [20].

2.2. Solid state structure of *1a*

Ortep view of **1a** is shown in Fig. 3. Bond length and bond angle data correspond to the expected values. The absolute configuration of **1a** is: C5:*R*, C8:*R*, C9:*S*, C10:*S*

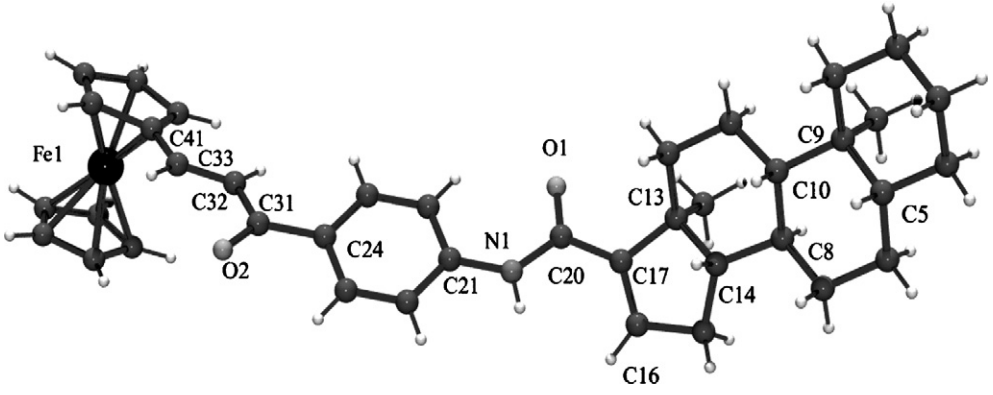


Fig. 3. Ortep view of **1a** at 50% probability level with partial numbering scheme. Selected bond length (Å) and torsion angle (°) data: Fe–C 1.994–2.054; C20–N1 1.351(11); C33–C32 1.330(12); C32–C31 1.464(13); C31–O2 1.233(12); C21–N1 1.392(10); C20–O1 1.227(11); O1–C20–N1–C21 −5; O2–C31–C32–C33 10; C25–C24–C31–O2 17; C13–C17–C20–N1 −152; C13–C16–C20–O1 27.

C13:*S*, C14:*S*. The central moiety is close to planar because of delocalisation, restricted rotation is possible around the C17–C20, C32–C31 and C33–C41 bonds. The C41–C31–C33 plane is rotated with respect to the C41 Cp ring and C21 phenyl by 7° and 36°, respectively. The ferrocene moiety is directed by ~100° upwards and the steroid skeleton ~140° downwards from the central planar part of the molecule. Steric hindrance prevents formation of hydrogen bond with N1–H as hydrogen donor. Search of the Cambridge Structural Database [21] (CSD, Version 5.27, May 2006) shows only two hits for steroids substituted by and amide group at the C17 position (Refcodes TUXCEU and VUZKEG).

3. Conclusions

Steroids bearing a ferrocene-containing moiety in the 17 or 3 positions can effectively be synthesised by the palladium-catalysed carbonylation of the corresponding steroidal alkenyl iodides or enol triflates. According to the X-ray study, in structure **1a** no classic hydrogen bond is formed with the amide group in the solid phase.

4. Experimental

4.1. Synthesis of chalcone *6*

1-(4′-Aminophenyl)-3-ferrocenyl-prop-2-en-1-one (**6**) was prepared by condensation of ferrocenecarboxaldehyde (2.14 g, 10 mmol) with 4′-amino-acetophenone (1.35 g, 10 mmol) in ethanol (10 ml), applying 10% aqueous KOH solution (8.4 g) as base catalyst. Purification was made by column chromatography (silica gel, MeOH–EtOAc 1:1 → 9:1) to give homogeneous product. Recrystallisation from MeOH gave purple crystals (2.25 g, 68%), mp 218–220 °C, lit. mp 210–213 °C [15]. MS (*m*/*z*/rel. int.): 331(M^+)/60; 266/100; 180/20; 121/20.

4.2. General procedure for the preparation of steroidal ferrocenyl chalcones (*1a*–*4a*)

In a typical experiment a mixture of 0.24 mmol of the steroidal substrate, 0.01 mmol $Pd(OAc)_2$, 0.02 mmol PPh_3, 0.2 mmol of **6** and 100 μl Et_3N was heated in a CO atmosphere in 2 ml dioxane at 100 °C for 16 h. The reaction was monitored by TLC. After completion of the reaction the solvent was removed in vacuo. The products were isolated by column chromatography (silica gel, eluent: toluene/ethanol = 50/3).

4.3. Physical measurements

^1H- and ^{13}C NMR spectra were recorded on a VARIAN INOVA 400 spectrometer at 400 and 100.58 MHz, respectively. 70 eV EI MS measurements were performed on a FISONS TRIO 1000 spectrometer using direct inlet. IR spectra were made using an Avatar 330 FT-IR instrument. Samples were prepared as KBr pellets. Elemental analyses were measured on a 1108 Carlo Erba apparatus.

4.3.1. 17-(N-(4′-((2-Ferrocenyl-ethenyl)-carbonyl)-phenyl)carbamoyl)-5α-androst-16-ene (*1a*)

^1H NMR ($CDCl_3$) δ: 8.00 (d, $J = 8.2$ Hz, 2H); 7.72 (d, $J = 15.5$ Hz, 1H); 7.67 (d, $J = 8.2$ Hz, 2H); 7.55 (br s, 1H); 7.11 (d, $J = 15.5$ Hz, 1H); 6.50 (m, 1H); 4.60 (br s, 2H); 4.45 (br s, 2H); 4.18 (s, 5H); 2.4–1.2 (m, 22H, steroid ring protons); 1.06 (s, 3H); 0.82 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 188.3; 164.0; 151.2; 146.4; 146.3; 141.9; 137.5; 134.0; 129.8; 119.0; 118.9; 79.4; 71.3; 69.8; 69.0; 56.8; 55.2; 47.3; 47.0; 38.5; 36.5; 35.0; 33.9; 32.0; 29.7; 29.0; 28.9; 26.8; 22.1; 20.7; 16.6; 12.2. MS (*m*/*z*/rel. int.): 615(M^+)/70; 550/10; 266/60; 121/100. IR (KBr, cm^{-1}): 3423; 1670; 1652. Anal. Calc. for $C_{39}H_{45}FeNO_2$ (615.64): C, 76.09; H, 7.37; N, 2.27. Found: C, 76.45; H, 7.12; N, 2.11%. Yield: 56%.

4.3.2. 17-(N-(4′-((2-Ferrocenyl-ethenyl)-carbonyl)-phenyl)carbamoyl)-3-methoxy-estra-1,3,5(10),16-tetraene (*2a*)

^1H NMR ($CDCl_3$) δ: 8.00 (d, $J = 8.8$ Hz, 2H); 7.70 (d, $J = 15.3$ Hz, 1H); 7.65 (d, $J = 8.8$ Hz, 2H); 7.60 (br s, 1H); 7.17 (d, $J = 9$ Hz, 1H); 7.15 (d, $J = 15.3$ Hz, 1H); 6.69 (dd, $J = 9$ Hz, $J = 3$ Hz, 1H); 6.62 (d, $J = 3$ Hz, 1H); 6.58 (m, 1H); 4.80 (br s, 2H); 4.49 (br s, 2H); 4.20 (s, 5H); 3.77 (s, 3H); 2.9–0.8 (m, 13H, steroid ring protons); 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 188.3; 163.9; 157.5; 151.1; 146.4; 146.3; 141.9; 137.7; 137.1; 134.0; 132.5; 129.7; 126.1; 119.0; 118.9; 113.9; 111.4; 79.3; 71.3; 69.8; 69.0; 55.8; 55.2; 47.3; 44.2; 37.0; 34.8; 31.8; 29.6; 27.7; 26.4; 16.5. MS (*m*/*z*/rel. int.): 625(M^+)/100; 560/20; 331/10; 292/35; 266/50; 121/90; 91/50. IR (KBr, cm^{-1}): 3416; 1668; 1653. Anal. Calc. for $C_{39}H_{39}FeNO_3$ (625.59): C, 74.88; H, 6.28; N, 2.24. Found: C, 75.05; H, 6.49; N, 2.04%. Yield: 43%.

4.3.3. 17-(N-(4′-((2-Ferrocenyl-ethenyl)-carbonyl)-phenyl)carbamoyl)-6α-hydroxy-3α,5α-cycloandrost-16-ene (*3a*)

^1H NMR ($CDCl_3$) 7.98 (d, $J = 8.7$ Hz, 2H); 7.75 (d, $J = 15.3$ Hz, 1H); 7.65 (d, $J = 8.77$ Hz, 2H); 7.56 (br s, 1H); 7.12 (d, $J = 15.3$ Hz, 1H); 6.51 (m, 1H); 4.60 (br s, 2H); 4.47 (br s, 2H); 4.18 (s, 5H); 3.32 (m, 1H); 2.38–0.8 (m, 17H, steroid ring protons); 1.10 (s, 3H); 1.08 (s, 3H); 0.55 (m, 1H); 0.30 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 188.3; 163.9; 151.1; 146.4; 146.3; 141.8; 137.3; 134.0; 129.8; 119.0; 118.9; 79.3; 73.5; 71.3; 69.8; 68.9; 56.7; 48.1; 47.1; 43.1; 39.1; 36.9; 35.0; 32.9; 32.0; 28.2; 24.9; 24.3; 22.3; 20.1; 16.7; 11.6. MS (*m*/*z*/rel. int.): 611($M^+ - H_2O$)/100; 546/20; 292/50; 266/70; 121/75; 105/70; 91/100. IR (KBr, cm^{-1}): 3434; 1667; 1651. Anal. Calc. for $C_{39}H_{43}FeNO_3$ (629.62): C, 74.40; H, 6.88; N, 2.22. Found: C, 74.19; H, 6.61; N, 2.37%. Yield: 55%.

4.3.4. 3-(N-(4′-((2-Ferrocenyl-ethenyl)-carbonyl)-phenyl)carbamoyl)-17β-(3″-methyl-pentan-1″,5″-diyl)carboxamido-androsta-3,5-diene (**4a**)

8.00 (d, $J = 8.4$ Hz, 2H); 7.72 (d, $J = 15.1$ Hz, 1H); 7.65 (d, $J = 8.4$ Hz, 2H); 7.61 (br s, 1H); 7.15 (d, $J = 15.1$ Hz, 1H); 6.9 (s, 1H); 5.85 (m, 1H); 4.64 (m, 2H); 4.60 (br s, 2H); 4.48 (br s, 2H); 4.2 (s, 5H); 4.05 (m, 2H); 3.05–0.9 (m, 23H, steroid ring protons); 0.97 (s, 3H); 0.92 (s, 3H); 0.8 (d, 6 Hz, 3H). IR (KBr, cm^{-1}): 3418; 1653; 1635. Anal. Calc. for $C_{46}H_{54}FeN_2O_3$ (738.79): C, 74.78; H, 7.37; N, 3.79. Found: C, 74.41; H, 7.12; N, 3.66%. Yield: 75%.

4.4. X-ray structure

Deep orange crystal ($0.35 \times 0.25 \times 0.1$ mm) of **1a** was fixed on a glass capillary using epoxy glue. Data were collected at 293(1) K, Bruker-Nonius MACH3 diffractometer, Mo Kα radiation $\lambda = 0.71073$ Å, ω motion, $\theta_{max} = 26.05°$ [22]. The structure was solved using the SIR-92 software [23] and refined on F^2 using SHELX-97 [24] program, publication material was prepared with the WINGX-97 suite [25]. Hydrogen atoms were fixed into geometric position except the amide hydrogen which could be found at the difference electron density map.

Acknowledgments

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Appendix A. Supplementary material

CCDC 619190 contains the supplementary crystallographic data for **1a**. The data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.034.

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[22] Crystal data for **1a**: Formula $C_{39}H_{45}FeNO_2$, $M = 615.61$, triclinic, space group $P1$, $a = 6.060(2)$ Å, $b = 6.271(5)$ Å, $c = 21.275(2)$ Å, $\alpha = 88.14(1)°$, $\beta = 89.52(2)°$, $\gamma = 73.92(1)°$, $V = 776.4(7)$ Å^3, $Z = 1$, $\rho_{calc} = 1.317$, 3479 measured, 2450 reflections were unique with $I > 2\sigma(I)$, decay: 16%, $R_1 = 0.0679$ and $wR_2 = 0.1753$ for all data, GOF = 1.038, 3479, 388 parameters. Residual electron density: 0.807/−0.670 e/Å^3.
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