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DIASTEREOTOPIC SYNTHESIS OF 1- AND 1,1-SUBSTITUTED 4-PHENYL-2,3,4,9-TETRAHYDRO-1H-β-CARBOLINES

B. B. Semenov,[1] K. A. Novikov,[1] A. N. Spitsin,[1] V. N. Azev,[2] and V. V. Kachala[3]

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A diastereotopic Pictet—Spengler reaction was performed to form previously unknown 1- and 1,1-substituted 4-phenyl-β-carbolines based on β-phenyltryptamine, aldehydes of various structure, and isatins. It has been demonstrated that the predominant diastereomers of the prepared β-carbolines have the (R,R*) configuration. The diasteroselectivity (de) of the reaction varies from 44 to 88%.*

Key words: β-carbolines, β-phenyltryptamine, Pictet—Spengler reaction, diastereoselective synthesis, eleagnine, harmane alkaloids.

The Pictet—Spengler reaction, which occurs in plants and in humans, leads to the formation of various derivatives including isoquinoline and β-carboline.

Some very simple alkaloids containing the β-carboline structural moiety and belonging to the harmane group are found in medicinal plants such as *Passiflora fluidum* [1], *P. edulis*, *P. incarnata*, *Bansteriopsis caapi* [2], and *Peganum harmala* [3], Zygophylaceae. They are used in traditional medicine to treat asthma, jaundice, and other diseases [3, 4]. Harmaline is a known MAO inhibitor and powerful serotonin antagonist [5]. Harmane alkaloids have been detected in food plants [2] such as soy, rye, wheat, rice, barley, mushrooms, grape juice, wine [6], charred insects, and cigarette smoke. It has been reported that alcohol increases the harmane content in the brain and urine [7].

Cytotoxic effects of harmane alkaloids have also been found [8]. These alkaloids are reported to affect the cardiovascular system [9, 10] and to have a hypotensive effect [10].

The harmane alkaloids include also eleagnine [(1*R*)-1-methyl-2,3,4,9-tetrahydro-1H-β-carboline].

A synthesis of the racemate of eleagnine (**1a**) using the Pictet—Spengler reaction based on tryptamine (**1**) and acetaldehyde was previously proposed [11].

Much later eleagnine was biosynthesized [12] and synthesized enantioselectively [13, 14] and (1*S*)-1-methyl-2,3,4,9-tetrahydro-1H-β-carboline was synthesized enantioselectively (ee > 98%) [15]. The reaction proceeded through the formation of two diastereomers with subsequent fractional crystallization of one of them and removal of a sulfamide, which was known to be chiral.

Recently the solid-phase chemistry of indole is rapidly developing with the Pictet—Spengler reaction being carried out on a polymeric support to synthesize 1,3-disubstituted β-carbolines. Diastereoselectivities (de) of 8-52% have been obtained from tryptophan [16-25]. It depended on the presence of a substituted nitrogen in the indole ring [20].

Based on this, we carried out diastereotopic syntheses of previously unknown 4-phenyl-1- and 1,1-substituted β-carboline derivatives using the Pictet—Spengler reaction. The starting materials were β-phenyltryptamine (**1**) as the racemate and aliphatic, aromatic, and heterocyclic aldehydes.

1) D. I. Mendeleev Russian Chemical Engineering University, 125047, Moscow, Miusskaya pl. 9, fax (7095) 200 42 04, e-mail: semenovb@mail.ru; 2) Tufts University, Medford, 02155, USA, e-mail: vazev02@tufts.edu; 3) Institute of Organic Chemistry, Russia, Moscow, e-amil: kachala@ioc.ac.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 481-485, November-December, 2004. Original article submitted July 26, 2004.

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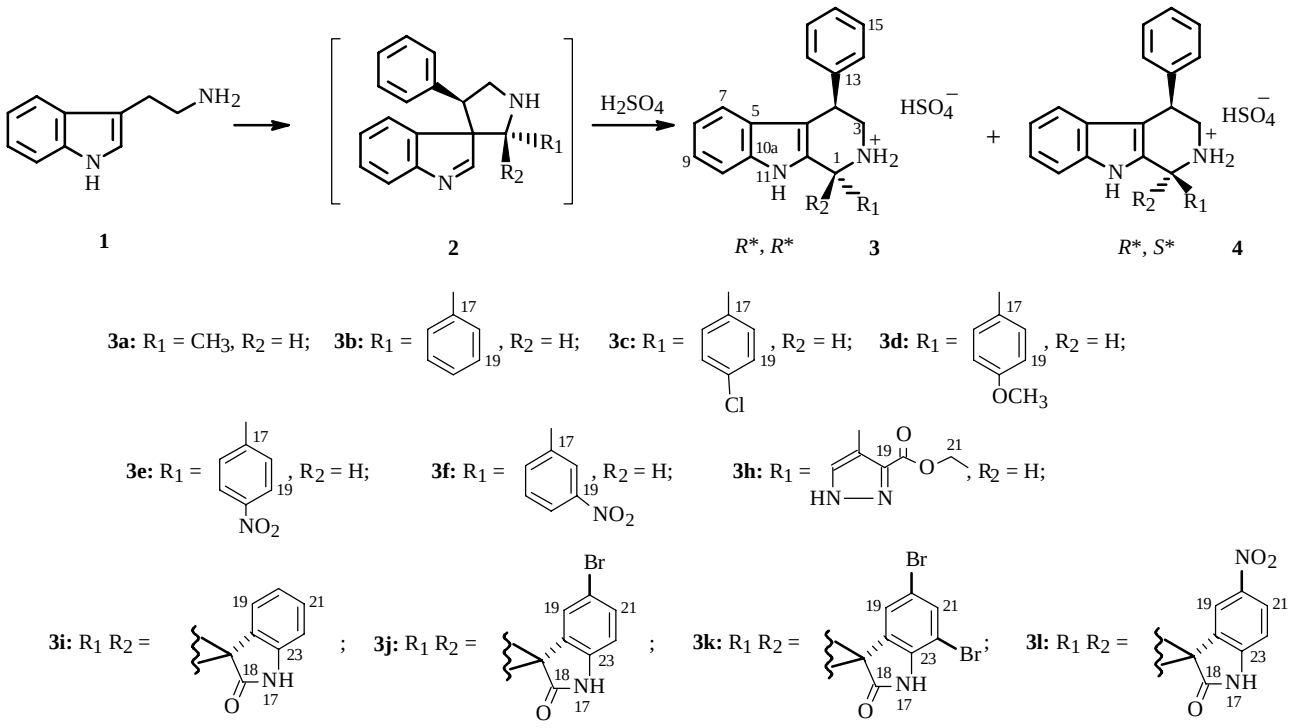
TABLE 1. PMR Chemical Shifts for **3a-f** and **4a-f**, ppm

Proton	Compound											
	3a (1R*,4R*)	**4a** (1S*, 4R*)	**3b** (1R*, 4R*)	**4b** (1S*, 4R*)	**3c** (1R*, 4R*)	**4c** (1S*, 4R*)	**3d** (1R*, 4R*)	**4d** (1S*, 4R*)	**3e** (1R*, 4R*)	**4e** (1S*, 4R*)	**3f** (1R*, 4R*)	**4f** (1S*, 4R*)
1-H	4.91	4.75	5.89	5.76	5.75	5.58	5.76	5.60	5.89	5.70	5.92	5.75
2-H	-	-	-	-	-	-	-	-	-	-	-	-
3-H	3.79	3.56	3.67	3.41	3.59	3.37	3.60	3.39	3.60	3.40	3.65	3.40
	3.20	3.22	3.38	2.85	3.16	2.82	3.19	2.89	3.17	2.81	3.20	2.82
4-H	4.55	4.41	4.60	4.46	4.51	4.36	4.61	4.42	4.51	4.37	4.56	4.39
7-H	6.53	6.58	6.58	6.69	6.59	6.69	6.59	6.72	6.64	a	6.61	a
8-H	6.76	6.78	6.74	6.80	6.74	6.79	6.74	6.80	6.78	a	6.76	a
9-H	7.04	7.08	6.99	7.03	6.98	7.01	6.97	7.00	6.99	a	6.99	a
10-H	7.40	7.40	7.27	7.32	7.25	7.30	7.31	7.36	7.26	a	7.25	a
11-H	11.33	11.29	10.76	11.02	10.71	10.94	10.67	10.94	10.74	10.99	10.77	11.02
14-H	7.28	7.31	7.29	7.35	7.30	7.32	7.30	7.30	7.31	a	7.29	a
15-H	7.35	7.35	7.35	a	7.32	7.32	7.30	7.30	7.33	a	7.33	a
16-H	7.35	7.35	7.31	a	7.32	7.32	7.26	7.26	7.37	a	7.29	a
17-H	1.61	1.64	-	-	-	-	-	-	-	-	-	-
18-H	-	-	7.43	7.44	7.45	7.45	7.38	7.30	7.68	8.06	8.30	a
19-H	-	-	7.49	a	7.56	7.51	7.00	7.02	8.30	8.39	-	-
20-H	-	-	7.44	a	-	-	-	-	-	-	8.31	a
21-H	-	-	-	-	-	-	3.78	3.76	-	-	-	-

[a]Signal not assigned.



Scheme 1

TABLE 2. ^{13}C NMR Chemical Shifts for **3a-f** and **4a-f**, ppm

C atom	Compound											
	3a (1R*, 4R*)	**4a** (1S*, 4R*)	**3b** (1R*,4R*)	**4b** (1S*,4R*)	**3c** (1R*,4R*)	**4c** (1S*,4R*)	**3d** (1R*,4R*)	**4d** (1S*,4R*)	**3e** (1R*,4R*)	**4e** (1S*,4R*)	**3f** (1R*,4R*)	**4f** (1S*,4R*)
C-1	49.0	47.3	56.9	54.6	55.9	54.0	56.5	54.6	56.0	a	56.0	a
C-3	48.5	44.9	49.7	46.2	50.6	47.3	50.3	47.1	49.9	a	50.1	a
C-4	37.4	36.8	38.4	38.2	39.6	39.6	38.8	38.9	38.7	a	39.2	a
C-5	108.2	107.3	110.4	110.3	110.6	109.2	110.5	110.4	110.6	a	110.7	a
C-6	125.0	125.0	125.2	a	125.7	126.2	125.6	125.8	125.3	a	125.4	a
C-7	118.8	118.8	118.9	118.8	118.7	118.5	118.9	118.7	118.8	a	118.8	a
C-8	118.8	118.8	118.7	118.7	118.3	118.4	118.7	118.8	118.6	a	118.6	a
C-9	121.4	121.5	121.3	121.3	120.8	120.8	121.3	121.4	121.2	a	121.2	a
C-10	111.4	111.4	111.6	111.6	111.3	111.5	111.6	111.5	111.4	a	111.4	a
C10a	136.4	136.3	136.6	136.5	136.3	136.4	136.7	136.6	136.5	a	136.5	a
C-12	132.0	132.5	131.7	a	134.1	133.7	133.0	133.4	132.0	a	132.1	a
C13	140.3	140.3	141.4	a	142.8	141.5	142.0	142.7	141.9	a	141.9	a
C-14	128.2	128.2	128.4	128.4	128.2	128.2	128.4	128.4	128.3	a	128.3	a
C-15	128.3	128.3	128.4	a	128.2	128.2	128.4	128.4	128.3	a	128.3	a
C-16	127.3	127.2	127.1	a	126.5	126.7	127.0	126.8	126.8	a	126.8	a
C-17	16.7	17.9	a	a	139.1	a	129.7	129.7	145.6	a	139.9	a
C-18	-	-	129.6	a	131.1	129.3	130.7	130.5	130.7	a	123.9	a
C-19	-	-	129.3	a	128.3	128.3	114.2	114.1	123.6	a	147.8	a
C-20	-	-	129.3	a	a	a	159.8	159.5	147.7	a	123.6	a
C-21	-	-	-	-	-	-	55.4	55.8	-	-	-	-

[a]Signal not assigned.

TABLE 3. PMR Chemical Shifts for **3h-l** and **4h-l**, ppm

Proton	Compound									
	3h (1R*,4R*)	**4h** (1S*,4R*)	**3i** (1R*,4R*)	**4i** (1S*,4R*)	**3j** (1R*,4R*)	**4j** (1S*,4R*)	**3k** (1R*,4R*)	**4k** (1S*,4R*)	**3l** (1R*,4R*)	**4l** (1S*,4R*)
1-H	5.78	5.70	-	-	-	-	-	-	-	-
3-H	3.41	3.22	3.79	3.44	3.97	3.16	3.37	3.03	3.41	3.06
	2.80	2.78	4.13	3.98	3.88	3.63	3.63	4.02	3.71	4.03
4-H	4.24	4.19	4.80	4.68	4.57	4.40	4.37	4.29	4.45	4.34
7-H	6.70	6.61	6.58	6.70	6.59	6.83	6.62	6.93	6.60	6.95
8-H	6.75	6.79	6.77	6.82	6.76	6.83	6.73	6.82	6.75	6.85
9-H	6.94	7.01	7.03	7.08	7.01	7.04	6.97	7.03	6.98	7.03
10-H	7.28	7.35	7.25	7.28	7.23	7.23	7.20	7.21	7.18	7.20
11-H	10.51	10.78	10.97	11.08	10.88	10.91	10.76	10.81	10.76	10.81
14-H	7.28	7.28	7.41	7.40	7.38	7.38	7.33	7.33	7.35	7.35
15-H	7.28	7.28	7.40	7.40	7.38	7.38	7.32	7.32	7.35	7.35
16-H	7.21	7.20	7.33	7.34	7.31	7.31	7.25	7.25	7.28	7.26
17-H	7.51	7.47	11.31	11.28	11.14	11.02	11.08	10.99	11.41	11.25
19-H	-	-	7.45	7.43	7.47	7.36	7.33	7.28	8.06	7.91
20-H	-	-	7.13	7.15	-	-	-	-	-	-
21-H	4.34	4.28	7.52	7.46	7.62	7.54	7.75	7.73	8.33	8.29
22-H	1.30	1.32	7.16	7.20	7.04	6.98	-	-	7.21	7.18

TABLE 4. ^{13}C NMR Chemical Shifts for **3h-l** and **4h-l**, ppm

C atom	Compound									
	3h (1R*,4R*)	**4h** (1S*,4R*)	**3i** (1R*,4R*)	**4i** (1S*,4R*)	**3j** (1R*,4R*)	**4j** (1S*,4R*)	**3k** (1R*,4R*)	**4k** (1S*,4R*)	**3l** (1R*,4R*)	**4l** (1S*,4R*)
C-1	47.8	46.1	59.7	60.3	60.2	61.3	61.9	62.2	60.4	60.9
C-3	49.7	45.0	45.2	46.8	46.2	47.3	47.8	47.4	47.5	47.5
C-4	38.7	38.6	37.1	37.2	38.3	38.3	39.8	38.5	39.4	38.1
C-5	108.9	108.5	112.0	111.9*	112.5	112.0	113.9	113.8	113.3	112.4
C-6	125.3	125.2	125.0	125.1*	125.2	125.5	125.6	125.5	125.5	125.8
C-7	118.4	118.6	119.2	119.1	119.1	118.8	119.0	118.6	119.0	118.6
C-8	118.0	118.3	119.0	119.0	118.9	118.8	118.5	118.5	118.5	118.5
C-9	120.2	120.6	122.2	122.2	121.9	121.7	121.4	121.5	121.4	121.4
C-10	111.2	111.4	111.7	111.7	111.6	111.5	111.4	111.4	111.3	111.3
C10a	136.9	136.5	136.8	136.8	136.6	136.6	136.4	136.4	136.4	136.4
C-12	131.7	131.6	127.5	127.6*	128.6	128.6	131.0	131.3	132.2	130.6
C-13	144.4	140.9	140.7	140.3	141.9	141.7	143.1	144.3	142.8	144.2
C-14	128.2	128.2	128.7	128.6	128.6	128.6	128.3	128.2	128.2	128.1
C-15	128.1	128.2	128.5	128.5	128.4	128.4	128.2	128.2	128.2	128.2
C-16	126.1	126.3	127.5	127.2	127.1	126.5	126.8	126.5	126.5	126.1
C-17	133.5	133.4	-	-	-	-	-	-	-	-
C-18	130.4	130.4	172.6	170.9*	174.3	173.1*	177.1	175.0	177.3	178.4
C-18a	-	-	124.9	126.6*	130.2	132.4*	134.8	135.9*	131.4	133.1
C-19	111.3	111.1	126.2	125.7	128.3	128.3	126.2	126.1	120.6	119.8
C-20	161.8	161.8	122.8	122.7	114.0	114.0	114.0	113.9	142.3	142.2
C-21	60.2	60.2	131.7	131.2	133.6	132.7	134.1	133.9	126.9	126.5
C-22	14.1	14.1	111.2	111.6	112.7	112.5	103.4	103.5	110.4	110.3
C-23	-	-	143.1	142.7	142.3	142.0	141.8	141.8	149.3	149.3

*Signal may be inaccurately assigned.

The diastereoselectivity is known to be determined either by electronic or steric factors [26]. Therefore, the substituents in the 2- and 4-positions of the pyrrolidine ring in intermediate **2** should be as far from each other as possible, i.e., have the *trans*-orientation. The Pictet—Spengler reaction was proved to proceed through spiro intermediate **2** using isotopic labeling [27]. Primarily the (R^*,R^*) diastereomers **3** (Scheme 1) are formed during the rearrangement of **2** into the β-carboline system apparently because of these same steric factors.

Compounds **3** and **4** are mixtures of two diastereomers with predominance of the R^*,R^* diastereomer (**a**, de 44%; **b**, 70%; **c**, 62%; **d**, 63%; **e**, 62%; **f**, 56%; **h**, 66%; **i**, 88%; **j**, 72%; **k**, 72%; **l**, 66%).

The ratio of diastereomers (de) was found by comparing the integrated intensities of H-3, H-3a, and H-4 in PMR spectra of the prepared compounds. Their structures were studied using one- (1D) and two-dimensional (2D) NMR spectroscopy. Two sets of signals of different intensity corresponding to two diastereomers were observed in 1D PMR and ^{13}C NMR spectra. The signals were assigned by analyzing 2D COSY, TOCSY, HSQC, and HMBC spectra. The three-dimensional structure of each diastereomer was found using 2D H—H NOE (NOESY) spectroscopy to determine closely positioned protons. Tables 1-4 give chemical shifts in PMR and ^{13}C NMR spectra for **3** and **4**.

The compounds were named using IUPAC rules and the program ACD Lab.

EXPERIMENTAL

NMR spectra were recorded on a DRX-500 (Bruker) instrument at working frequencies 500.13 and 125.76 MHz for ^{1}H and ^{13}C, respectively, in DMSO-d_6 at 30°C using standard Bruker methods. 2D HSQC and HMBC spectra were obtained

using a gradient method. TMS was used as an internal standard. Mass spectra were recorded in an SSQ-710 (Finnigan MAT) spectrometer at 70 eV ionizing-electron energy. Elemental analyses agreed with those calculated.

β-Phenyltryptamine (1). A mixture of 3-(2-nitro-1-phenylethyl)indole (26.6 g, 0.1 mol) [28] in alcohol (94%, 100 mL) and freshly prepared Raney nickel (1 g) was treated over 60 h with hydrazine hydate (50 mL) in alcohol (100 mL). If the boiling stopped, then a new portion of catalyst was added. The mixture was filtered. The filtered catalyst was washed with hot alcohol (3 × 10 mL). The filtrate was evaporated. The solid was dissolved in anhydrous ether and treated with ether saturated with HCl. The resulting hydrochloride was filtered off, suspended in ether, and shaken with aqueous base. The ether solution was dried over $MgSO_4$ and evaporated.

Yield 21 g (90%), mp 131-132°C (lit. mp 131-132°C [28]) (from ethylacetate).

General Method for Preparing 3 and 4. A mixture of **1** (1 g, 0.005 mol) in water (40 mL) and aldehyde or isatin (0.72 g, 0.0043 mol) was treated with conc. H_2SO_4 (1 g) and boiled for 60 h. The solid sulfates of **3** and **4** were filtered off and crystallized from aqueous alcohol. The base was obtained by slurrying the sulfates with an excess of aqueous potash.

This method produced:

3a and **4a** based on acetaldehyde and 1-methyl-4-phenyl-2,3,4,9-tetrahydro-β-carboline 1-sulfate.

Yield 50%, mp 218°C (sulfate), *m*/*z* (I_{rel}, %): 262 (10) $[M]^+$.

3b and **4b** based on benzaldehyde and 1,4-diphenyl-2,3,4,9-tetrahydro-β-carboline 1-sulfate.

Yield 60%, mp 228°C (sulfate), *m*/*z* (I_{rel}, %): 324 (14) $[M]^+$.

3c and **4c** based on *p*-chlorobenzaldehyde and 4-phenyl-1-(4-chlorophenyl)-2,3,4,9-tetrahydro-β-carboline 1-sulfate.

Yield 63%, mp 255°C (sulfate), *m*/*z* (I_{rel}, %): 358 (14) $[M]^+$.

3d and **4d** based on *p*-methoxybenzaldehyde and 1-(4-methoxyphenyl)-4-phenyl-2,3,4,9-tetrahydro-β-carboline 1-sulfate.

Yield 55%, mp 225°C (sulfate), *m*/*z* (I_{rel}, %): 354 (20) $[M]^+$.

3e and **4e** based on *p*-nitrobenzaldehyde and 1-(4-nitrophenyl)-4-phenyl-2,3,4,9-tetrahydro-β-carboline 1-sulfate.

Yield 80%, mp >260°C (sulfate), *m*/*z* (I_{rel}, %): 369 (30) $[M]^+$.

3f and **4f** based on *m*-nitrobenzaldehyde and 1-(3-nitrophenyl)-4-phenyl-2,3,4,9-tetrahydro-β-carboline 1-sulfate.

Yield 76%, mp >260°C (sulfate), *m*/*z* (I_{rel}, %): 369 (27) $[M]^+$.

3h and **4h** based on ethyl 4-formyl-1H-pyrazol-3(5)-carboxylate [32] and ethyl 4-(4-phenyl-2,3,4,9-tetrahydro-1H-β-carbolin-1-yl)-1H-pyrazol-3(5)-carboxylate 1-sulfate.

Yield 87%, mp 255°C (sulfate), *m*/*z* (I_{rel}, %): 386 (10) $[M]^+$.

3i and **4i** based on 1 H-indole-2,3-dione and 4-phenyl-2,3,4,9-tetrahydrospiro[β-carboline-1,3′-indole]-2′(1′H)-one 1-sulfate.

Yield 46%, mp >300°C. Mass spectrum (EI, 70 eV) *m*/*z* (I_{rel}, %): 365 (10) $[M]^+$.

3j and **4j** based on 5-bromo-1H-indole-2,3-dione [33] and 5′-bromo-4-phenyl-2,3,4,9-tetrahydrospiro[β-carboline-1,3′-indole]-2′(1′H)-one 1-sulfate.

Yield 60%, mp 263°C (dec.). Mass spectrum (EI, 70 eV) *m*/*z* (I_{rel}, %): 444 (15) $[M]^+$.

5,7-Dibromo-1H-indole-2,3-dione. A mixture of isatin (30 g) and conc. H_2SO_4 (80 mL) was treated with bromine (40 g) at <0°C with vigorous stirring, held at that temperature for 1 h, left overnight allowing the temperature to rise to ambient, treated with glacial acetic acid (300 mL) and bromine (40 g), boiled until the bromine disappeared, poured onto ice, and filtered. The solid was suspended with aqueous potash and washed with water until the washings were neutral to afford the product, yield 59 g, 95%, mp 253°C (lit. mp 252°C [30a]).

3k and **4k** based on 5,7-dibromo-1H-indole-2,3-dione [33] and 5′,7′-dibromo-4-phenyl-2,3,4,9-tetrahydrospiro[β-carboline-1,3′-indole]-2′(1′H)-one 1-sulfate.

Yield 76%, mp >300°C. Mass spectrum (EI, 70 eV) *m*/*z* (I_{rel}, %): 523 (15) $[M]^+$.

3l and **4l** based on 5-nitro-1H-indole-2,3-dione [30b] and 5′-nitro-4-phenyl-2,3,4,9-tetrahydrospiro[β-carboline-1,3′-indole]-2′(1′H)-one 1-sulfate.

Yield 39%, mp 246°C. Mass spectrum (EI, 70 eV) *m*/*z* (I_{rel}, %): 410 (15) $[M]^+$.

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