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REACTION OF ANALOGS OF NATURAL ISOFLAVONOIDS WITH AMIDINES

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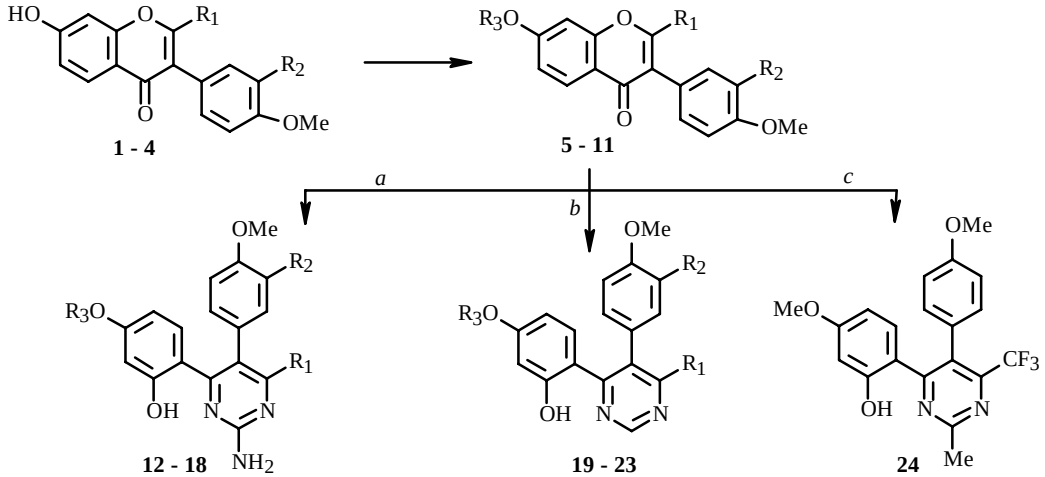
Recyclization of the chromone ring in a series of analogs of natural isoflavonoids by reaction with amidines was studied.

Key words: isoflavonoids, chromone ring, recyclization, amidines.

In continuation of research on the synthesis and reactivity of natural alkoxyisoflavones (formononetin, orobol, biochanin A, pseudobaptigenin, cladrin) and their analogs and considering the high and varied biological activity of isoflavonoids, we studied the reaction of these compounds with amidines. The pyrimidine ring appears in the B vitamins and nitrogeneous bases, which are important components of nucleic acids, nucleosides, and nucleotides, and in cofactors and enzymes. Sulfanilamide preparations, which possess bacteriostatic activity (sulfazine, sulfadimesine, sulfadimethoxine, et al.) and are synthetic derivatives of pyrimidine, are broadly used in medical practice [1].

Isoflavones are known to recyclize into the corresponding 4-(2-hydroxyphenyl)pyrimidine derivatives upon reaction with amidines in ethanol in the presence of sodium ethoxide [2-5] or in DMSO in the presence of potash under a N_2 atmosphere [6].

The susceptibility of isoflavonoids to attack by nucleophilic reagents depends on their structure. The presence of electron-accepting substituents, especially in the 3-position of the chromone ring, significantly enhances the reaction. Electron-donating methoxyls in the B ring of analogs of natural isoflavones markedly decreases the reactivity of the latter to attack by nucleophilic reagents. The presence of substituents in the 2-position of the chromone ring sometimes significantly lowers the product yields and prolongs the reaction time (especially for flavones).



a. $H_2NC(=NH)NH_2$; *b.* $HC(=NH)NH_2$; *c.* $MeC(=NH)NH_2$

1, 4 - 7, 11 - 14, 18 - 21, 23: R_1 = H; **2, 8, 9, 15, 16:** R_1 = Me; **3, 10, 17, 22:** R_1 = CF_3; **1 - 3, 5 - 10, 12 - 17, 19 - 22**: R_2 = H; **4, 11, 18, 23:** R_2 = OMe; **5, 8, 10, 12, 15, 17, 19, 22:** R_3 = Me; **6, 9, 11, 13, 16, 18, 20, 23:** R_3 = $MeC(=CH_2)CH_2$; **7, 14, 21:** R_3 = 4-$MeC_6H_4CH_2$

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Natural isoflavonoids are most often encountered in nature as hydroxylated, methoxylated, or glycosylated derivatives. The presence in them of several electron-donating groups has a great influence on their reactivity. Therefore, it was interesting to study the reaction conditions of analogs of natural isoflavones with common amidines of acids, e.g., guanidine, formamidine, and acetamidine.

As it turned out, the reaction of alkoxy derivatives of formononetin and cladrin **5-11** with amidines in ethanol in the presence of NaOEt did not give the desired results owing to the duration of the reaction and the low yield of desired pyrimidines.

Considering the structural features of the studied compounds, the recyclization of the chromone ring was carried out in DMF in the presence of potash in order to prepare the corresponding substituted pyrimidines in high yield. Under these conditions, we obtained substituted 4-(2-hydroxyphenyl)pyrimidines **12-24** in yields of 73-87%. The duration of the reaction of the isoflavones with the amidines depended strongly on their nucleophilicity. Thus, recyclization of the chromone ring via reaction with guanidinium carbonate took 4-6 h; with formamidinium acetate, 8-10 h; with acetamidinium chloride, up to 20 h with heating was required to complete the reaction.

Under these conditions, recyclization of 2-trifluoromethyl substituted isoflavones proceeded more readily due to the presence of the electron-accepting substituent directly at the reaction center. However, the presence of an electron-donating 2-methyl decreased the reactivity of C-2 toward amidines. In this instance, satisfactory yields of the desired pyrimidines could be obtained only by reaction with the most nucleophilic guanidine.

The products **12-24** were soluble in aqueous bases, which is typical of phenols. The synthesized 4-(2-hydroxyphenyl)pyrimidines gave a yellow color with $TiCl_4$ in alcohol, which is indicative of an intramolecular H-bond between the phenol hydroxyl and a N atom of the pyrimidine ring.

PMR spectra of **12-24** agreed completely with their structures. A characteristic feature of the spectra was the separate absorption of the OH and NH_2 protons as a result of slow proton exchange. Thus, a 2H slightly broadened singlet for the amino group was observed at 6.85-7.01 ppm; of the 2-hydroxyl, at 11.4-14.0 ppm.

Thus, we studied the reactivity of derivatives of formononetin and cladrin toward amidines of acids. The rate of recyclization of the chromone ring depended on both the isoflavone structure and the reactivity of the binucleophile.

EXPERIMENTAL

The course of reactions and purity of products were monitored by TLC on Sorbfil UV-254 (Russia) and Merck (Germany) plates with elution by $CHCl_3$:CH_3OH (95:5 and 9:1). PMR spectra were measured on a VXR-300 instrument (Varian, 300 MHz) in DMSO-d_6 relative to TMS (internal standard) on the δ-scale. Elemental analyses of all compounds agreed with those calculated.

Starting isoflavones **1-5**, **8**, and **10** were prepared as before [7-11].

General Method for Synthesizing 7-Alkoxyisoflavones 6, 7, 9, and 11. A hot solution of the appropriate 7-hydroxyisoflavone (10 mmol, **1**, **2**, or **4**) in absolute acetone (30 mL) was treated with freshly calcined potash (2.1 g, 15 mmol), stirred, boiled, and treated with the corresponding alkylhalide (12 mmol). The reaction mixture was held for 1-4 h (end of reaction determined by TLC) and poured into acidified icewater (100 mL). The resulting precipitate was filtered off and crystallized from a suitable solvent.

7-[(2-Methylprop-2-enyl)oxy]-3-(4-methoxyphenyl)-4*H*-chromen-4-one (6). $C_{20}H_{18}O_4$, yield 75%, mp 116-118°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.79 (3H, s, OMe-4′), 6.99 (2H, d, ^3J = 8.2, H-3′, H-5′), 7.10 (1H, dd, ^4J = 2, ^3J = 8, H-6), 7.16 (1H, d, ^4J = 2, H-8), 7.53 (2H, d, ^3J = 8.2, H-2′, H-6′), 8.04 (1H, d, ^4J = 2, H-5), 8.41 (1H, s, H-2); alkyl protons: 1.80, 5.01, 5.11, 4.64 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-7].

7-[(4-Methylbenzyl)oxy]-3-(4-methoxyphenyl)-4*H*-chromen-4-one (7). $C_{24}H_{20}O_4$, yield 87%, mp 163-165°C (propan-2-ol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.79 (3H, s, OMe-4′), 6.99 (2H, d, ^3J = 8.2, H-3′, H-5′), 7.13 (1H, dd, ^3J = 8, ^4J = 2, H-6), 7.24 (1H, d, ^4J = 2, H-8), 7.53 (2H, d, ^3J = 8.2, H-2′, H-6′), 8.04 (1H, d, ^3J = 8, H-5), 8.41 (1H, s, H-2); alkyl protons: 2.31 (3H, s, Me-4), 5.21 (2H, s, CH_2O-7), 7.22 (2H, d, ^3J = 8, H-3, H-5), 7.38 (2H, d, ^3J = 8, H-2, H-6).

2-Methyl-7-[(2-methylprop-2-enyl)oxy]-3-(4-methoxyphenyl)-4*H*-chromen-4-one (9). $C_{21}H_{20}O_4$, yield 81%, mp 112-114°C (ethanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.26 (3H, s, Me-2), 3.80 (3H, s, OMe-4′),

6.99 (2H, d, ^{3}J = 8.2, H-3′, H-5′), 7.06 (1H, dd, ^{4}J = 2, ^{3}J = 8, H-6), 7.11 (1H, d, ^{4}J = 2, H-8), 7.20 (2H, d, ^{3}J = 8.2, H-2′, H-6′), 7.94 (1H, d ^{4}J = 2, H-5); alkyl protons: 1.80, 5.01, 5.10, 4.64 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-7].

3-(3,4-Dimethoxyphenyl)-7-[(2-methylprop-2-enyl)oxy]-4*H*-chromen-4-one (11). $C_{21}H_{20}O_5$, yield 70%, mp 120-122°C (ethanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.80 (6H, s, OMe-3′, OMe-4′), 7.00 (1H, d, ^{3}J = 8.4, H-5′), 7.10 (1H, dd, ^{3}J = 8, ^{4}J = 2.4, H-6), 7.14 (1H, d, ^{4}J = 2.4, H-8), 7.15 (1H, dd, ^{3}J = 8.4, ^{4}J = 2.0, H-6′), 7.16 (1H, d, ^{4}J = 2.0, H-2′), 8.05 (1H, d, ^{3}J = 8, H-5), 8.43 (1H, s, H-2); alkyl protons: 1.80, 5.02, 5.11, 4.65 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-7].

General Method for Synthesizing Substituted 4-(2-Hydroxyphenyl)pyrimidines 12-24. A solution of 7-alkoxyisoflavone (**5-11**, 10 mmol) in DMF (25 mL) was treated with freshly calcined potash (5.5 g, 40 mmol) and amidinium salt (20 mmol). The reaction mixture was stirred at 75-80°C for 4-20 h (end of reaction determined by TLC), poured into water (100-150 mL), and acidified with dilute HCl until the pH was 6. The precipitate was filtered off, dried, and crystallized from methanol.

2-[2-Amino-5-(4-methoxyphenyl)pyrimidin-4-yl]-5-methoxyphenol (12). $C_{18}H_{17}N_3O_3$, yield 78%, mp 119-121°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.70, 3.75 (6H, 2s, OMe-5, OMe-4′), 6.15 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.38 (1H, d, ^{4}J = 2.0, H-6), 6.87 (1H, d, ^{3}J = 8.0, H-3), 6.90 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.11 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 12.36 (1H, s, OH-1); pyrimidine protons: 6.89 (2H, s, NH_2-2), 8.16 (1H, s, H-6).

2-[2-Amino-5-(4-methoxyphenyl)pyrimidin-4-yl[-5-[(2-methylprop-2-enyl)oxy]phenol (13). $C_{21}H_{21}N_3O_3$, yield 87%, mp 152-154°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74, 4.93, 5.02, 4.40 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-5], 3.76 (3H, s, OMe-4′), 6.17 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.39 (1H, d, ^{4}J = 2.0, H-6), 6.86 (1H, d, ^{3}J = 8.0, H-3), 6.90 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.11 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 12.30 (1H, s, OH-1); pyrimidine protons: 6.99 (2H, s, NH_2-2), 8.16 (1H, s, H-6).

2-[2-Amino-5-(4-methoxyphenyl)pyrimidin-4-yl]-5-[(4-methylbenzyl)oxy]phenol (14). $C_{25}H_{23}N_3O_3$, yield 75%, mp 190-192°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.30, 7.15, 4.99 (3H, s, 4H, m, 2H, s, $MeC_6H_4CH_2$O-5), 3.75 (3H, s, OMe-4′), 6.20 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.44 (1H, d, ^{4}J = 2.0, H-6), 6.86 (1H, d, ^{3}J = 8.0, H-3), 6.90 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.29 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 12.29 (1H, s, OH-1); pyrimidine protons: 6.90 (2H, s, NH_2-2), 8.17 (1H, s, H-6).

2-[2-Amino-6-methyl-5-(4-methoxyphenyl)pyrimidin-4-yl]-5-methoxyphenol (15). $C_{19}H_{19}N_3O_3$, yield 75%, mp 209-212°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.66, 3.76 (6H, 2s, OMe-5, OMe-4′), 6.00 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.30 (1H, d, ^{4}J = 2.0, H-6), 6.66 (1H, d, ^{3}J = 8.0, H-3), 6.93 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.06 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 12.85 (1H, s, OH-1); pyrimidine protons: 2.05 (3H, s, Me-6), 6.88 (2H, s, NH_2-2).

2-[2-Amino-6-methyl-5-(4-methoxyphenyl)pyrimidin-4-yl]-5-[(2-methylprop-2-enyl)oxy]phenol (16). $C_{22}H_{23}N_3O_3$, yield 73%, mp 180-181°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.71, 4.91, 4.99, 4.37 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-5], 3.77 (3H, s, OMe-4′), 6.03 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.33 (1H, d, ^{4}J = 2.0, H-6), 6.66 (1H, d, ^{3}J = 8.0, H-3), 6.93 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.07 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 12.83 (1H, s, OH-1); pyrimidine protons: 2.05 (3H, s, Me-6), 6.89 (2H, s, NH_2-2).

2-[2-Amino-5-(4-methoxyphenyl)-6-trifluoromethylpyrimidin-4-yl]-5-methoxyphenol (17). $C_{19}H_{16}F_3N_3O_3$, yield 85%, mp 215-216°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.63, 3.71 (6H, 2s, OMe-5, OMe-4′), 6.15 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.27 (1H, d, ^{4}J = 2.0, H-6), 6.78 (1H, d, ^{3}J = 8.0, H-3), 6.81 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.05 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 7.35 (2H, s, NH_2-2 of pyrimidine), 10.51 (1H, s, OH-1).

2-[2-Amino-5-(3,4-dimethoxyphenyl)pyrimidin-4-yl]-5-[(2-methylprop-2-enyl)oxy]phenol (18). $C_{22}H_{23}N_2O_4$, yield 78%, mp 190-192°C (ethanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74, 4.93, 5.00,4.42 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-5], 3.60, 3.75 (6H, 2s, OMe-3′, OMe-4′), 6.20 (1H, dd, ^{3}J= 8.0, ^{4}J = 2.0, H-4), 6.38 (1H, d, ^{4}J = 2.0, H-6), 6.89 (1H, d, ^{3}J = 8.0, H-3), 6.75 (1H, d, ^{4}J = 2.0, H-2′, 6.74 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-6′), 6.91 (1H, d, ^{3}J = 8.0, H-5′), 12.15 (1H, s, OH-1); pyrimidine protons: 6.94 (2H, s, NH_2-2), 8.22 (1H, s, H-6).

5-Methoxy-2-[5-(4-methoxyphenyl)pyrimidin-4-yl]phenol (19). $C_{18}H_{16}N_2O_3$, yield 76%, mp 128-130°C (ethanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.70, 3.75 (6H, 2s, OMe-5, OMe-4′), 6.37 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.32 (1H, d, ^{4}J = 2.0, H-6), 7.08 (1H, d, ^{3}J = 8.0, H-3), 6.90 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.20 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 10.34 (1H, s, OH-1); pyrimidine protons: 8.70 (1H, s, H-6), 9.12 (1H, s, H-2).

5-[(2-Methylprop-2-enyl)oxy]-2-[5-(4-methoxyphenyl)pyrimdin-4-yl]phenol (20). $C_{21}H_{20}N_2O_3$, yield 78%, mp 196-197°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75, 4.95, 5.03, 4.41 [3H, 1H, 1H, 2H, 4s,

MeC(=CH_2)CH_2O-5], 3.75 (3H, s, OMe-4′), 6.33 (1H, d, ^{4}J = 2.0, H-6), 6.39 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.90 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.08 (1H, d, ^{3}J = 8.0, H-3), 7.20 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 10.30 (1H, s, OH-1); pyrimidine protons: 8.71 (1H, s, H-6), 9.12 (1H, s, H-2).

5-[(4-Methylbenzyl)oxy]-2-[5-(4-methoxyphenyl)pyrimidin-4-yl]phenol (21). $C_{25}H_{22}N_2O_3$, yield 87%, mp 185-187°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.30, 7.20, 5.00 (3H, s, 4H, m, 2H, s, Me$C_6H_4CH_2$O-5), 3.75 (3H, s, OMe-4′), 6.39 (1H, d, ^{4}J = 2.0, H-6), 6.44 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.90 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.09 (1H, d, ^{3}J = 8.0, H-3), 7.30 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 10.35 (1H, s, OH-1); pyrimidine protons: 8.70 (1H, s, H-6), 9.11 (1H, s, H-2).

5-Methoxy-2-[5-(4-methoxyphenyl)-6-trifluoromethylpyrimidin-4-yl]phenol (22). $C_{19}H_{15}F_3N_2O_3$, yield 82%, mp 130-131°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.66, 3.73 (6H, 2s, OMe-5, OMe-4′), 6.29 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.26 (1H, d, ^{4}J = 2.0, H-6), 6.95 (1H, d, ^{3}J = 8.0, H-3), 6.85 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.12 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 9.38 (1H, s, H-2 of pyrimidine), 9.79 (1H, s, OH-1).

2-[5-(3,4-Dimethoxyphenyl)pyrimidin-4-yl]-5-[(2-methylprop-2-enyl)oxy]phenol (23). $C_{22}H_{22}N_2O_4$, yield 80%, mp 123-125°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75, 4.94, 5.01, 4.42 [3H, 1H, 1H, 2H, 4s, MeC(=CH_2)CH_2O-5], 3.55, 3.75 (6H, 2s, OMe-3′, OMe-4′), 6.35 (1H, d, ^{4}J = 2.0, H-6), 6.41 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.81 (1H, d, ^{4}J = 2.0, H-2′), 6.86 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-6′), 6.94 (1H, d, ^{3}J = 8.0, H-5′), 7.09 (1H, d, ^{3}J = 8.0, H-3), 10.27 (1H, s,OH-1); pyrimidine protons: 8.77 (1H, s, H-6), 9.12 (1H, s, H-2).

5-Methoxy-2-[5-(4-methoxyphenyl)-2-methyl-6-trifluoromethylpyrimidin-4-yl]phenol (24). $C_{20}H_{17}F_3N_2O_3$, yield 74%, mp 202-203°C (methanol). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.77 (3H, s, Me-2 of pyrimidine), 3.65, 3.72 (6H, 2s, OMe-5, OMe-4′), 6.27 (1H, dd, ^{3}J = 8.0, ^{4}J = 2.0, H-4), 6.25 (1H, d, ^{4}J = 2.0, H-6), 6.91 (1H, d, ^{3}J = 8.0, H-3), 6.83 (2H, d, ^{3}J = 8.0, H-3′, H-5′), 7.09 (2H, d, ^{3}J = 8.0, H-2′, H-6′), 9.85 (1H, s, OH-1).

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