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THE SYNTHESIS OF 6-R-2,2,4-TRIMETHYL-1,2-DIHYDROQUINOLINE- AND 6-R-4-R'-2,2,4-TRIMETHYL-1,2,3,4-TETRAHYDROQUINOLINE-8-CARBOXYLIC ACIDS – THE STRUCTURAL ANALOGUES OF HELQUINOLINE

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Key words: pyrrolo[3,2,1-ij]quinoline-1,2-diones; oxidation; 6-R-2,2,4-trimethyl-1,2-dihydroquinoline-8-carboxylic acid; 6-R-4-R'-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acid

The peculiarities of the oxidation reaction of substituted (5,6-dihydro)-4,4,6-trimethyl-4H-pyrrolo[3,2,1-ij] quinoline-1,2-diones have been investigated. 6-R-2,2,4-trimethyl-1,2-dihydroquinoline-8-carboxylic acids and 6-R-4-R'-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acids, which are structural analogues of the natural antibiotic Helquinoline ((2R,4S)-4-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acid), have been obtained by oxidation of 8-R-4,4,6-trimethyl-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diones and their hydrogenated analogues – 8-R-6-R'-4,4,6-trimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diones. It has been shown that 8-R-6-R'-4,4,6-trimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diones and 8-R-4,4,6-trimethyl-4H-pyrrolo [3,2,1-ij]quinoline-1,2-diones are oxidized similar to isatin with opening of the pyrrole-1,2-dione fragment and subsequent decarboxylation, and the presence of bulky substituents – gem-dimethyl groups in the second position of the hydroquinoline cycle has no steric effect on the process. Moreover, it has been found that oxidation of 8-R-4,4,6-trimethyl-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diones proceeds selectively with opening the pyrrole-1,2-dione fragment without affecting the multiple bond of the dihydroquinoline cycle, polymerization also does not occur on it. The structure of 6-R-4-R'-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acids and 6-R-2,2,4-trimethyl-1,2-dihydroquinoline-8-carboxylic acids has been confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. With the help of mass spectroscopy it has been shown that the heterocyclic fragment of 6-R-2,2,4-trimethyl-1,2-dihydroquinoline-8-carboxylic acids is more stable compared to the fragment of 6-R-4-R'-2 2,4-trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acids.

СИНТЕЗ 6-R-2,2,4-ТРИМЕТИЛ-1,2-ДИГІДРОХІНОЛІН- І 6-R-4-R'-2,2,4-ТРИМЕТИЛ-1,2,3,4-ТЕТРАГІДРОХІНОЛІН-8-КАРБОНОВИХ КИСЛОТ – СТРУКТУРНИХ АНАЛОГІВ HELQUINOLINE
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Ключові слова: *пірол[3,2,1-ij]хінолін-1,2-діон; окиснення; 6-R-2,2,4-триметил-1,2-дигідрохінолін-8-карбонова кислота; 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагідрохінолін-8-карбонова кислота*
Досліджені особливості реакції окиснення в ряду заміщених (5,6-дигідро)-4,4,6-триметил-4Н-піроло[3,2,1-ij] хінолін-1,2-діонів. Окисненням 8-R-4,4,6-триметил-4Н-піроло[3,2,1-ij]хінолін-1,2-діонів і їх гідрованих аналогів 8-R-6-R'-4,4,6-триметил-5,6-дигідро-4Н-піроло[3,2,1-ij]хінолін-1,2-діонів отримані відповідно 6-R-2,2,4-триметил-1,2-дигідрохінолін-8-карбонові кислоти та 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагідрохінолін-8-карбонові кислоти, що є структурними аналогами природного антибіотика Helquinoline ((2R, 4S)-4-метокси-2-триметил-1,2,3,4-тетрагідрохінолін-8-карбонової кислоти). Показано, що 8-R-6-R'-4,4,6-триметил-5,6-дигідро-4Н-піроло[3,2,1-ij]хінолін-1,2-діони і 8-R-4,4,6-триметил-4Н-піроло[3,2,1-ij]хінолін-1,2-діони окиснюються подібно ізатину з розкриттям пірол-1,2-діонового фрагменту і подальшим декарбоксилюванням, причому наявність у другій позиції гідрохінолінового циклу об'ємних заступників – гем-диметильних груп не чинить стеричного впливу на цей процес. Крім того, встановлено, що окиснення 8-R-4,4,6-триметил-4Н-піроло[3,2,1-ij]хінолін-1,2-діонів протікає селективно з розкриттям пірол-1,2-діонового фрагменту, не зачіпаючи кратну зв'язку дигідрохінолінового циклу, полімеризація по ній також не відбувається. Будову 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагідрохінолін-8-карбонових кислот і 6-R-2,2,4-триметил-1,2-дигідрохінолін -8-карбонових кислот підтверджено даними ЯМР ^{1}H та ЯМР ^{13}C спектроскопії, мас-спектрометрії та елементного аналізу. За допомогою мас-спектроскопії показано, що більшою стабільністю володіє гетероциклічний фрагмент 6-R-2,2,4-триметил-1,2-дигідрохінолін-8-карбонових кислот у порівнянні з фрагментом 6-R-4-R'-2, 2,4-триметил-1,2,3,4-тетрагідрохінолін-8-карбонових кислот.

СИНТЕЗ 6-R-2,2,4-ТРИМЕТИЛ-1,2-ДИГИДРОХИНОЛИН- И 6-R-4-R'-2,2,4-ТРИМЕТИЛ-1,2,3,4-ТЕТРАГИДРОХИНОЛИН-8-КАРБОНОВЫХ КИСЛОТ – СТРУКТУРНЫХ АНАЛОГОВ HELQUINOLINE
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Ключевые слова: *пирроло[3,2,1-ij]хинолин-1,2-дионы; окисление; 6-R-2,2,4-триметил-1,2-дигидрохинолин-8-карбоновая кислота; 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагидрохинолин-8-карбоновая кислота*
Изучены особенности реакции окисления в ряду замещенных (5,6-дигидро)-4,4,6-триметил-4Н-пирроло [3,2,1-ij]хинолин-1,2-дионов. Окислением 8-R-4,4,6-триметил-4Н-пирроло[3,2,1-ij]хинолин-1,2-дионов и их гидрированных аналогов 8-R-6-R'-4,4,6-триметил-5,6-дигидро-4Н-пирроло[3,2,1-ij]хинолин-1,2-дионов получены соответственно 6-R-2,2,4-триметил-1,2-дигидрохинолин-8-карбоновые кислоты и 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагидрохинолин-8-карбоновые кислоты, являющиеся структурными ана-

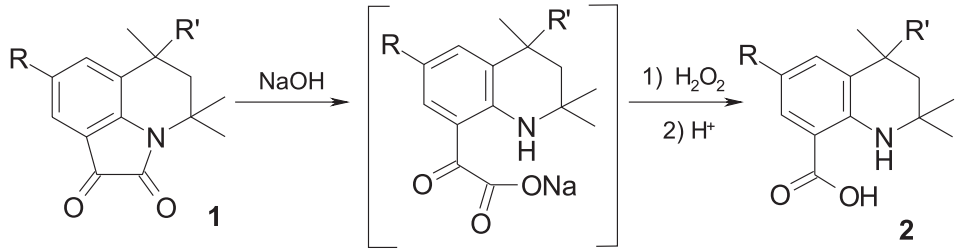
логами природного антибиотика Helquinoline ((2R,4S)-4-метокси-2-метил-1,2,3,4-тетрагидрохинолин-8-карбоновой кислоты). Показано, что 8-R-6-R'-4,4,6-триметил-5,6-дигидро-4H-пирроло[3,2,1-ij]хинолин-1,2-дионы и 8-R-4,4,6-триметил-4H-пирроло[3,2,1-ij]хинолин-1,2-дионы окисляются подобно изатину с раскрытием пиррол-1,2-дионового фрагмента и последующим декарбоксилированием, причем наличие во втором положении гидрохинолинового цикла объемных заместителей – гем-диметильных групп не оказывает стерического влияния на этот процесс. Кроме того, установлено, что окисление 8-R-4,4,6-триметил-4H-пирроло[3,2,1-ij]хинолин-1,2-дионов протекает селективно с раскрытием пиррол-1,2-дионового фрагмента, не затрагивая кратную связь дигидрохинолинового цикла, полимеризация по ней также не происходит. Строение 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагидрохинолин-8-карбоновых кислот и 6-R-2,2,4-триметил-1,2-дигидрохинолин-8-карбоновых кислот подтверждено данными ЯМР ^{1}H и ЯМР ^{13}C спектроскопии, масс-спектрометрии и элементного анализа. С помощью масс-спектроскопии показано, что большей стабильностью обладает гетероциклический фрагмент 6-R-2,2,4-триметил-1,2-дигидрохинолин-8-карбоновых кислот по сравнению с фрагментом 6-R-4-R'-2,2,4-триметил-1,2,3,4-тетрагидрохинолин-8-карбоновых кислот.

The fragment of tetrahydroquinoline carboxylic acid is the structural moiety of a wide range of natural quinoline alkaloids such martinellic acid isolated from the root bark of the South American plant *Martinella iquitosensis* and a new natural antibiotic *Helquinoline* ((2R, 4S) -4-methoxy-2-methyl-1,2, 3,4-tetrahydro-8-quinolinecarboxylic acid) obtained from *Janibacter limosus Hel* [1-5]. It is also present in the structure of some synthetic medicinal products (antibiotic of a new generation virantmycin [6, 7], oxamniquine [8] used to treat schistosomiasis, etc.). In particular, hydroquinoline-8-carboxylic acids possess the antirheumatic, antibacterial activity [4, 9]. At the same time derivatives of 2,2,4-trimethyl-1,2-dihydroquinolines and their hydrogenated analogues – substituted 2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines [10-12] exhibit a broad spectrum of the biological activity. In this connection the synthesis of 2,2,4-trimethyl-1,2-dihydroquinoline and 2,2,4-trimethyl-1,2, 3,4-tetrahydroquinoline-8-carboxylic acids being the structural analogues of the natural antibiotic *Helquinoline* is of interest. In addition, these aromatic amino acids are good building blocks for constructing new heterocyclic compounds, including with the properties of surfactants.

One of the most effective methods for the synthesis of substituted anthranilic acids is oxidation of various 1*H*-indole-2,3-dione (isatins) with hydrogen peroxide in the aqueous solution of alkalies [13, 14]. In the cause of this reaction isatins undergo disclosure of the pyrrole ring and are converted into salts of isatoic acid decarboxylated when reacting with an oxidizing agent. The structure of various 4,4,6-trimethyl-4*H*-pyrrolo[3,2,1-*ij*]quinoline-1,2-diones [15] earlier synthesized by us and the structure of isatin contain the pyrrol-1,2-dione fragment, which can be subjected to oxidation, but the presence of *gem*-dimethyl groups may create steric hindrance for the attack of the carbon atom of the amide group by the hydroxide ion [16]. It has been found that like isatin the disclosure of the pyrrole-1,2-dione fragment and decarboxylation occur without difficulty for all 8-R-6-R'-4,4,6-trimethyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*] quinolin-1,2-diones **1a-f** under the action of hydrogen peroxide in the alkaline medium. The subsequent treatment with dilute hydrochloric acid leads to formation of 6-R-4-R'-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acids **2a-f** undescribed previously (Scheme 1).

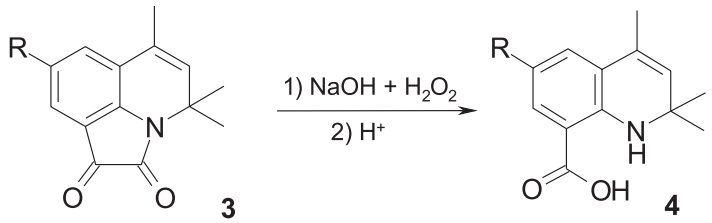
Similar interaction was conducted with hydrogen peroxide in the alkaline solution of 8-R-4,4,6-trimethyl-4*H*-pyrrolo[3,2,1-ij]quinoline-1,2-diones **3a-e**, containing the multiple bond in the heterocycle. It should be noted that for 1.2-dihydroquinolines polymerization is possible [17]. Furthermore, it is known that *N*-acyl-1,2-dihydroquinoline are oxidized with peroxides to form *N*-acyl-1,2-dihydroquinoline-3,4-epoxides [18], in which opening of the epoxide ring occurs under the action of bases [19]. It has been found that the oxidation reaction of pyrroloquinolinediones **3a-e** occurs selectively without affecting the multiple bond, and leads to 6-R-2,2,4-trimethyl-1,2-dihydroquinoline-8-carboxylic acids **4a-e**. Formation of polymerization products in this reaction is not detected (Scheme 2).

The structure of quinolinecarboxylic acid **2a-f** and **4a-e** has been unequivocally proven by the totality of the evidence of spectroscopy and spectrometry. The signals of protons of the secondary amino- and carboxyl groups are present in the ^{1}H NMR spectra of compounds **2a-f** and **4a-e** compared to the spec-



1, **2** R = H (a), Me (b, f), MeO (c), Et (d), F (e); R' = H (a-e), Ph (f)

Scheme 1



3, **4** R = H (a), Me (b), MeO (c), Et (d), F (e)

Scheme 2

tra of the starting pyrroloquinolinediones **1a-f** and **3a-e**. In the mass spectra (EI) of quinolinecarboxylic acids **2a-f** and **4a-e** the peaks of molecular ions with the low intensity (I_{rel} = 20-25%, I_{rel} = 10-17%, respectively) are observed; they are subjected to further fragmentation with emission of the methyl radical. The ions formed by sequential cleaving of molecular ions of the methyl radical and the molecule of H_2O have the maximum intensity (I_{rel} = 100%). In the spectra of 1,2-dihydroquinoline-8-carboxylic acids **4a-e** in contrast to the spectra 1,2,3,4-tetrahydroquinoline-8-carboxylic acids **2a-f** the fragment ions formed by sequential cleaving of molecular ions of the methyl radical, the molecule of H_2O and the molecule of CO (I_{rel} = 15-20%) are present. It indicates a greater stability of the 1,2-dihydroquinoline fragment compared to the 1,2,3,4-tetrahydroquinoline one.

Experimental Part

The ^{1}H NMR spectra and ^{13}C were recorded on a "Bruker AM-500" device (500 and 125 MHz, respectively) in the pulsed Fourier regime in $CDCl_3$, the position of signals of the test substances was determined by the δ-scale. The assignment of signals was carried out relative to the residual proton signals of the deuterium solvent. Mass spectra were recorded on a FINNIGAN MAT.INCOS spectrometer with the electron impact of 50 70 evc and direct input of the sample into the source of ions at 100-150°C and an accelerating voltage of 70 eV. Elemental analysis was performed on a Perkin Elmer 2400 device. The melting points were determined on a PTP-M device. Control of the individual reactants and the compounds obtained, as well as the course of the reaction was monitored by thin layer chromatography (TLC) on Merck TLC Silica gel 60 F254 plates (254-subscript) in the system of $CHCl_3$-EtOAc, 10:1. The starting compounds **1a-f** and 3**a-e** were synthesized by the procedure given earlier [15].

The general procedure for oxidation of 8-R-6-R'-4,4,6-trimethyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij] quinoline-1,2-diones 1a-f and 8-R-4,4,6-trimethyl-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diones 3a-e. Allow to stand 0.02 Mol of the corresponding pyrroloquinolinedione **1a-f** or **3a-e** in 20 ml of 20% aqueous solution of sodium hydroxide for 30 min, then while stirring and cooling add 0.04 Mol of hydrogen peroxide and mix at room temperature for 1.5-2 h. Pour the reaction mixture into 200 ml of water, neutralize with 10% HCl, filter the precipitate formed, wash with water, dry, crystallize from CCl_4 to give slightly yellow powders **2a-f** and **4a-e**.

2,2,4-Trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acid 2a. Yield – 2.0 g, 89%. M.p. – 167-168°C. ^{1}H NMR spectrum, δ, ppm: 1.27 (s, 3H, CH_3); 1.35 (s, 6H, C $(CH_3)_2$); 1.37 (d, J = 6.5 Hz, 1H, CH_2); 1.76 - 1.80 (m, 1H, CH_2); 2.91-2.96 (m, 1H, CH); 6.58 (t, J = 7.5 Hz, 1H, H-6 Ar); 7.33 (d, J = 7.5 Hz, 1H, H-5 Ar); 7.83 (d, J = 7.5 Hz, 1H, H-7, Ar); 9.50-10.20 (br.s., 1H, NH); 11.20-12.50 (br.s., 1H, OH). 13C NMR spectrum, δ, ppm: 20.0, 27.5, 29.2, 31.5, 43.1, 49.4, 107.2, 113.7, 126.9, 130.2, 132.0, 148.0, 174.2. MS: m/e (%) 219 ([M$^+$] (19)), 204 ([M-CH_3] (50)), 186 ([M-CH_3-H_2O] (100)). Found, %: C 71.31; H 7.79; N 6.47. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39.

2,2,4,6-Tetramethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acid 2b. Yield – 2.0 g, 82%. M.p. – 196-197°C. ^{1}H NMR spectrum, δ, ppm: 1.29 (s, 3H, CH_3); 1.35 (s, 6H, C $(CH_3)_2$); 1.37 (d, J = 6.8 Hz, 1H, CH_2); 1.80-1.84 (m, 1H, CH_2); 2.26 (s, 3H, 6-CH_3); 2.95-2.99 (m, 1H, CH); 7.20 (s, 1H, H-5 Ar); 7.26 (s, 1H, H-7, Ar); 9.80-10.40 (br.s., 1H, NH); 11.30-12.50 (br.s., 1H, OH). ^{13}C NMR spectrum, δ, ppm: 20.3, 27.5, 29.0, 31.4, 43.3, 49.4, 107.6, 123.2, 127.4, 129.5, 133.7, 145.6, 174.1. MS: m/e (%) 233 ([M$^+$] (24)), 218 ([M-CH_3] (50)), 200 ([M-CH_3-H_2O] (100)). Found, %: C 72.15; H 8.29; N 6.11. $C_{14}H_{19}NO_2$. Calculated, %: C 72.07; H 8.21; N 6.00.

2,2,4-Trimethyl-6-methoxy-1,2,3,4-tetrahydroquinoline-8-carboxylic acid 2c. Yield – 2.4 g, 92%. M.p. – 155-156°C. ^{1}H NMR spectrum, δ, ppm: 1.31 (s, 3H, CH3); 1.36 (s, 6H, C (CH3)2); 1.37 (d, J = 6.1 Hz, 1H, CH_2); 1.82-1.86 (m, 1H, CH_2);); 2.98-3.01 (m, 1H, CH); 3.78 (c, 3H, OCH_3); 7.00 (c, 1H, H-5 Ar); 7.34 (c, 1H, H-7, Ar); 9.40-10.20 (br.s., 1H, NH); 11.40-12.60 (br.s., 1H, OH). ^{13}C NMR spectrum, δ, ppm: 20.2, 28.2, 29.4, 31.7, 43.1, 49.5, 55.8, 107.3, 111.0, 123.5, 129.3, 143.0, 149.1, 173.7. MS: m/e (%) 249 ([M$^+$] (25)), 234 ([M-CH_3] (40)), 216 ([M-CH_3-H_2O] (100)). Found, %: C 67.61; H 7.57; N 5.54. $C_{14}H_{19}NO_3$. Calculated, %: C 67.45; H 7.68; N 5.62.

2,2,4-Trimethyl-6-ethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acid 2d. Yield – 2.3 g, 88%. M.p. – 157-158°C. ^{1}H NMR Spectrum, δ, ppm: 1.21 (t, J = 7.6 Hz, 3H, CH_3CH_2); 1.27 (s, 3H, CH_3); 1.34 (s, 6H, C $(CH_3)_2$); 1.37 (d, J = 6.6 Hz, 1H, CH_2); 1.77-

1.81 (m, 1H, CH_2); 2.54 (q, J = 7.6 Hz, 2H, CH_3CH_2); 2.93-2.96 (m, 1H, CH); 7.21 (s, 1H, H-5 Ar); 7.66 (s, 1H, H-7, Ar); 9.40-10.50 (br.s., 1H, NH); 11.10-12.30 (br.s., 1H, OH). ^{13}C NMR spectrum, δ, ppm: 15.8, 20.4, 27.6, 27.8, 29.1, 31.5, 43.3, 49.4, 107.2, 127.2, 128.3, 129.5, 132.5, 146.3, 174.1. MS: m/e (%) 247 ([M^+] (27)), 232 ([M-CH_3] (54)), 214 ([M-CH_3-H_2O] (100)). Found, %: C 72.98; H 8.44; N 5.75. $C_{15}H_{21}NO_2$. Calculated,%: C 72.84; H 8.56; N 5.66.

2,2,4-Trimethyl-6-fluoro-1,2,3,4-tetrahydroquinoline-8-carboxylic acid 2e. Yield – 2.0 g, 91%. M.p. – 172-173°C. ^{1}H NMR Spectrum, δ, ppm: 1.32 (c, 3H, CH_3); 1.37 (s, 6H, C $(CH_3)_2$); 1.38 (d, J = 6.2 Hz, 1H, CH_2); 1.86-1.90 (m, 1H, CH_2);); 2.99-3.02 (m, 1H, CH); 7.15 (s, 1H, H-5 Ar); 7.53 (s, 1H, H-7, Ar); 9.60-10.20 (br.s, 1H, NH); 11.40-12.70 (br.s, 1H, OH). ^{13}C NMR Spectrum, δ, ppm: 20.4, 28.4, 29.2, 31.7, 43.21, 50.8, 115.1, 116.5, 120.9, 122.2, 131.0, 147.1, 153.2, 173.2. MS: m/e (%) 237 ([M^+] (21)), 222 ([M - CH_3] (49)), 204 ([M-CH_3-H_2O] (100)). Found, %: C 77.81; H 7.48; N 4.63. $C_{14}H_{19}NO_3$. Calculated, %: C 77.65; H 7.49; N 4.53.

2,2,4,6-Tetramethyl-4-phenyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acid 2f. Yield – 2.4 g, 77%. M.p. – 205-206°C. ^{1}H NMR Spectrum, δ, ppm: 0.89 (s, 3H, C $(CH_3)_2$); 1.35 (s, 3H, C$(CH_3)_2$); 1.77 (s, 3H, CHs); 2.06-2.12 (m, 1H, CH_2); 2.24 (s, 3H, 6-CH_3); 2.38-2.43 (m, 1H, CH_2); 7.18 (s, 1H, H-5 Ar); 7.14-7.27 (m, 5H, Ph); 7.79 (s, 1H, H-7, Ar); 8.40-10.00 (br.s., 2H, NH, OH). ^{13}C NMR Spectrum, δ, ppm: 20.2, 27.7, 28.9, 31.3, 43.3, 49.5, 107.2, 123.4, 126.2, 127.6, 129.0, 129.5, 129.7, 133.7, 137.4, 145.0, 174.3. MS: m/e (%) 309 ([M^+] (22)), 294 ([M - CH_3] (38)), 276 ([M-CH_3-H_2O] (100)). Found, %: C 77.72; H 7.37; N 4.64. $C_{20}H_{23}NO_2$. Calculated,%: C 77.64; H 7.49; N 4.53.

2,2,4-Trimethyl-1,2-dihydroquinoline-8-carboxylic acid 4a. Yield – 1.9 g, 86%. M.p. – 174-175°C. ^{1}H NMR Spectrum, δ, ppm: 1.36 (s, 6H, C $(CH_3)_2$); 1.98 (s, 3H, CH_3); 5.38 (s, 1H, CH); 6.53 (t, J = 7.8 Hz, 1H, H-6 Ar); 7.19 (d, J = 7.8 Hz, 1H, H-5 Ar); 7.78 (d, J = 7.8 Hz, 1H, H-7, Ar); 8.90-9.20 (br.s, 1H, NH); 10.80-11.80 (br.s, 1H, OH). ^{13}C NMR Spectrum, δ, ppm: 19.0, 32.3, 52.0, 107.2, 114.2, 122.2, 127.4, 128.5, 128.9, 131.3, 131.4, 147.7, 174.0. MS: m/e (%) 217 ([M^+] (10)), 202 ([M-CH_3] (47)), 184 ([M-CH_3-H_2O] (100)), 156 ([M-CH_3-H_2O-CO] (15)). Found, %: C 72.01; H 7.06; N 6.40. $C_{13}H_{15}NO_2$. Calculated, %: C 71.87; H 6.96; N 6.45.

2,2,4,6-Tetramethyl-1,2-dihydroquinoline-8-carboxylic acid 4b. Yield – 2.0 g, 81%. M.p. – 197-198°C. ^{1}H NMR Spectrum, δ, ppm: 1.35 (s, 6H, C $(CH_3)_2$); 1.98 (s, 3H, CH_3); 2.22 (s, 3H, 6-CH_3); 5.39 (s, 1H, CH); 7.03 (s, 1H, H-5 Ar); 7.59 (s, 1H, H-7, Ar); 8.80-9.40 (br.s, 1H, NH); 10.50-11.20 (br.s, 1H, OH). ^{13}C NMR Spectrum, δ, ppm: 19.0, 20.4, 32.0, 51.9, 107.0, 122.4, 123.2, 127.5, 128.9, 130.3, 130.6, 130.7, 147.7, 174.0. MS: m/e (%) 231 ([M^+] (17)), 216 ([M-CH_3] (50)), 198 ([M-CH_3-H_2O] (100)), 170 ([M-CH_3-H_2O-CO] (21)). Found, %: C 72.82; H 7.52; N 6.13. C14H17NO2. Calculated, %: C 72.70; H 7.41; N 6.06.

2,2,4-Trimethyl-6-methoxy-1,2-dihydroquinoline-8-carboxylic acid 4c. Yield – 2.2 g, 87%. M.p. – 172-173°C. ^{1}H NMR Spectrum, δ, ppm: 1.39 (s, 6H, C $(CH_3)_2$); 2.00 (s, 3H, CH_3); 3.79 (s, 3H, OCH_3); 5.51 (s, 1H, CH); 6.93 (s, 1H, H-5 Ar); 7.30 (s, 1H, H-7, Ar); 9.00-9.20 (br.s, 1H, NH); 10.60-11.90 (br.s, 1H, OH). ^{13}C NMR Spectrum, δ, ppm: 19.0, 31.6, 32.3, 52.2, 55.9, 107.3, 111.4, 119.4, 124.6, 127.4, 130.3, 142.6, 149.5, 173.5. MS: m/e (%) 247 ([M^+] (14)), 232 ([M-CH_3] (58)), 214 ([M-CH_3-H_2O] (100)), 186 ([M-CH_3-H_2O-CO] (7)). Found, %: C 68.11; H 7.07; N 5.53. $C_{14}H_{17}NO_3$. Calculated, %: C 68.00; H 6.93; N 5.66.

2,2,4-Trimethyl-6-ethyl-1,2-dihydroquinoline-8-carboxylic acid 4d. Yield – 2.1 g, 84%. M.p. – 178-179°C. ^{1}H NMR Spectrum, δ, ppm: 1.21 (t, J = 7.6 Hz, 3H, CH_3CH_2); 1.37 (s, 6H, C $(CH_3)_2$); 2.01 (s, 3H, CH_3); 2.53 (q, J = 7.6 Hz, 2H, CH_3CH_2); 5.41 (s, 1H, CH); 7.08 (s, 1H, H-5 Ar); 7.52 (s, 1H, H-7, Ar); 8.00-8.90 (br.s, 1H, NH); 10.70-11.40 (br.s, 1H, OH). ^{13}C NMR Spectrum, δ, ppm: 15.8, 19.1, 28.0, 32.2, 52.1, 107.3, 122.6, 127.6, 128.8, 129.3, 129.5, 129.8, 130.2, 145.6, 173.9. MS: m/e (%) 245 ([M^+] (13)), 230 ([M-CH_3] (68)), 2128 ([M-CH_3-H_2O] (100)), 184 ([M-CH_3-H_2O-CO] (15)). Found, %: C 73.53; H 7.74; N 5.84. $C_{15}H_{19}NO_2$. Calculated, %: C 73.44; H 7.81; N 5.71.

2,2,4-Trimethyl-6-fluoro-1,2-dihydroquinoline-8-carboxylic acid 4e. Yield – 1.9 g, 78%. M.p. – 169-170°C. ^{1}H NMR Spectrum, δ, ppm: 1.38 (s, 6H, C $(CH_3)_2$); 1.97 (s, 3H, CH_3); 5.48 (s, 1H, CH); 6.96 (s, 1H, H-5 Ar); 7.44 (s, 1H, H-7, Ar); 8.70-9.00 (br.s, 1H, NH); 10.20-11.60 (br.s, 1H, OH). ^{13}C NMR Spectrum, δ, ppm: 19.1, 32.5, 52.1, 107.0, 114.1, 122.4, 127.2, 114.1, 129.0, 131.5, 147.6, 161.4, 174.5. MS: m/e (%) 235 ([M^+] (19)), 220 ([M-CH_3] (48)), 202 ([M-CH_3-H_2O] (100)), 174 ([M-CH_3-H_2O-CO] (23)). Found, %: C 72.82; H 7.52; N 6.13. $C_{13}H_{14}FNO_2$. Calculated, %: C 66.37; H 6.00; N 5.95.

Conclusions

1. It has been shown that 8-R-6-R'-4,4,6-trimethyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-1,2-diones and 8-R-4,4,6-trimethyl-4*H*-pyrrolo[3,2,1-*ij*] quinoline-1,2-diones are oxidized with hydrogen peroxide in the presence of alkali to form 6-R-4-R'-2,2 4-trimethyl-1,2,3,4-tetrahydroquinoline-8-carboxylic acids and 6-R-2,2,4-trimethyl-1,2-dihydroquinoline-8-carboxylic acids, respectively, and the presence of bulky substituents – gem-dimethyl groups in the second position of the hydroquinoline cycle has no steric effect on disclosure of the pyrrole-1,2-dione fragment and the subsequent decarboxylation.

2. It has been found that oxidation of 8-R-4,4,6-trimethyl-4H-pyrrolo[3,2,1-ij]quinoline-1,2-diones proceeds selectively with opening of the pyrrole-1,2-dione fragment without affecting the multiple bond of the dihydroquinoline cycle.

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