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SYNTHESIS OF SOME FLUROPHENYL 4-OXOCYCLOPENTANE[*d*]ISOXAZOLINES AND THEIR DIOXOLANE DERIVATIVES

A number of new fluorophenyl 4-oxocyclopentane[*d*]isoxazolines and their dioxolane derivatives has been synthesized. The obtained substances are of the interest as the perspective biologically active compounds as well as the intermediates in total synthesis of fluorinated prostaglandin analogues.

Introduction. Various cyclic β-di- and β-triketones are of interest as multifunctional compounds, while many of them show various biological activities [1–3]. The fluorine containing analogs of natural compounds are of particular importance [4–6], since the replacement of hydrogen atoms by fluorine due to the similarity of their sizes does not significantly change the steric structure of molecules [7].]. In the case of biologically active compounds this causes their complementarity with receptors, thus providing retention or enhancement of the biological properties of fluorinated analogs [1, 7]. As a rule their chemical and metabolic stability also increases. Therefore the development of the synthetic scheme for preparation of new analogs of cyclic β-triketones with fluorine containing side acyl chain is very actual.

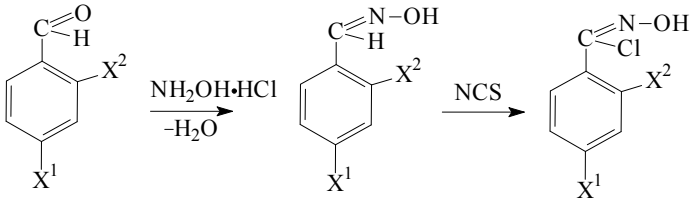
The aim of this work is to realize the scheme of synthesis of cyclic β-triketone analogs precursors with fluorine containing acyl side chain as synthons for the preparation of new fluorinated prostanoids [8, 9].

Main part. Within nitrile oxide approach new fluorine containing 3-aryl-4-oxocyclopentane-[*d*]isoxazolines have been obtained at the first step of this work via 1,3-dipolar cycloaddition reaction of unsaturated dipolarophiles and the corresponding nitrile oxides. There was used as dipolarophile 2-cyclopentenone which being synthesized in preparative amounts from dicyclopentadiene.

Hydroximoyl chlorides **3 a, b** (Scheme 1) were used as nitrile oxides precursors. In this connection, oximes **2 a, b** were synthesized from 2-fluoro- or 4- fluorobenzaldehyde **1 a, b** via the interaction of fluorine containing aromatic aldehydes with hydroxylamine hydrochloride (Scheme 1).

In the reaction conditions of 1,3-dipolar cycloaddition, hydroximoyl chlorides **3 a, b** were converted by action of triethylamine to nitrile oxides **4 a, b**, which were trapped in situ by 2-cyclopentenone (Scheme 2).

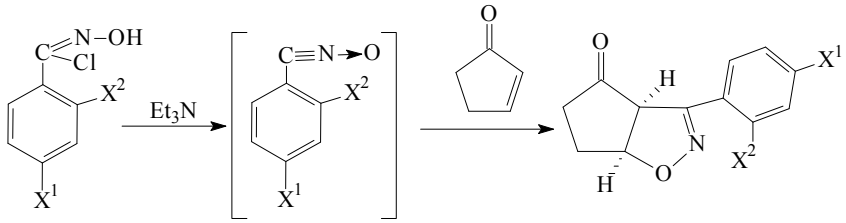
Cycloaddition reaction was carried out at room temperature, the products were isolated by column chromatography on silica gel (eluent: ether – light petroleum). As a result 4-oxo-3-(*o*-fluorophenyl)-44or 4-oxo-3-(*n*-fluorophenyl)-cyclopent[*d*]-isoxazolines **5 a, b** were isolated, the yield being 58.1 and 40.0%, respectively (Table).



1 **2** **3**

(**a**) X^1 = H, X^2 =F;
(**b**) X^1 = F, X^2 = H

Scheme 1

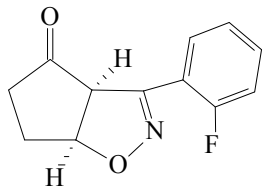
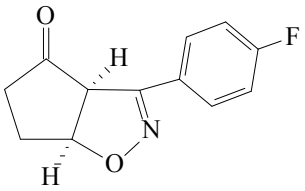
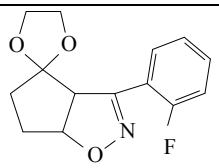
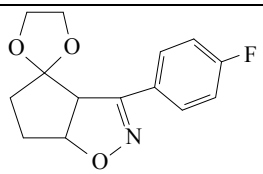


3 **4** **5**

(**a**) X^1 = H, X^2 =F;
(**b**) X^1 = F, X^2 = H

Scheme 2

Yields and physical properties of fluorine-containing condensed cyclopentane[*d*]isoxazolines and their dioxolane derivatives

Compound number	Structural formula	Molecular weight, M	Empirical formula	Yield, %	M.p., C°
5a		219.21	$C_{12}H_{10}FNO_2$	58.1	84–87
5b		219.21	$C_{12}H_{10}FNO_2$	40.0	134–137
6a		263.26	$C_{14}H_{14}FNO_3$	30.0	114–117
6b		263.26	$C_{14}H_{14}FNO_3$	50.5	115–118

The structure of the obtained products has been confirmed with the aid of modern physical-chemical methods of organic compounds analysis. The most characteristic signals for proof of the prepared isoxazoline **5 a** structure (Fig. 1) in the ^{1}H NMR spectrum are those of H-8 and H-12 (PG numeration of atoms is used to facilitate the spectral characteristics comparison).

Thus, the proton H-8 signal appears at 4.34 ppm as doublet with a spin-spin coupling constant J = 8.7 Hz. The signal as doublet of doublets in the 5.56 ppm region (J_1 = 8.7; J_2 = 5.2 Hz) corresponds to proton H-12. Chemical shifts and multiplicity of signals in ^{1}H NMR spectrum confirm the proposed structure **5 a**.

Thus, the shift of H-12 signal to a weaker field compared with H-8 signal is due to the more significant discreening influence of the isoxazoline oxygen atom than that of the cyclopentane carbonyl group.

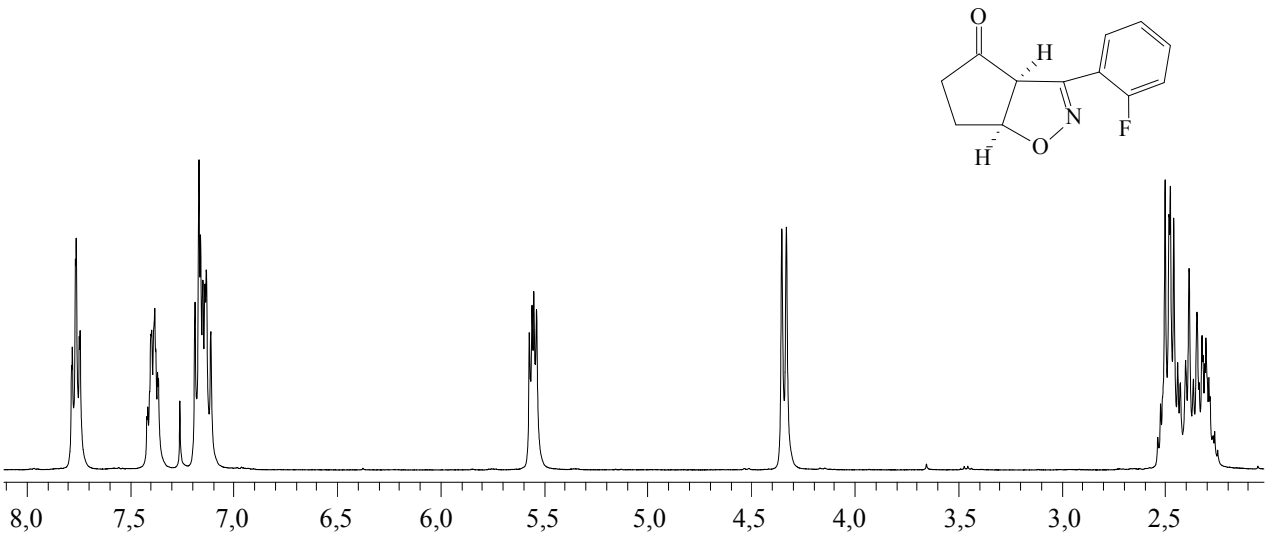


Fig. 1. ^{1}H NMR spectrum of 4-oxo-3-(2-fluorophenyl)cyclopenta[*d*]isoxazoline

Spin-spin coupling constant value (SSCC) of H-8 and H-12 (J_1 = 8.7 Hz) is in accordance with the *cis*-location of the corresponding protons, which confirms the stereospecificity of the 1,3-dipolar cycloaddition reaction proceeding via concerted mechanism.

The ^{1}H NMR spectrum of compound **5 b** contains similar protons signals corresponding to all the fragments present in the formula **5b**.

The assignment of all signals to appropriate C-atoms of the proposed structure has been accomplished for the ^{13}C NMR spectra of the synthesized condensed isoxazolines **5**.

The reaction was shown to proceed with a high regio- and stereoselectivity, i.e. the formation of neither regioisomeric nor stereoisomeric products was observed. This was confirmed by the absence of characteristic signals for these isomers in the ^{1}H NMR spectrum, recorded for the crude product after the initial treatment of the reaction mixture before chromatographic separation. Obviously, the major factor for the determining of high regioselectivity of dipolar cycloaddition reaction is electronic one, particularly when the posessing an increased electron density oxygen atom of nitrile oxide dipole forms bond with the most electrondificient β-carbon atom of C=C bond of dipolarophile which is α,β-unsaturated ketone.

Cis-stereochemistry of cycloaddition products are in good accordance with data obtained by consideration of the isoxazolines stereochemical models having been created using the CS ChemDraw 3D program, for example for compounds **5 a** and **6 a** (see Fig. 2 and 3).

In the developed synthetic scheme for preparation of new analogues of bioactive cyclic β-triketones with fluorine containing side acyl chain the transformation of isoxazoline precursors to target synthons is accomplished by heterocycle reductive cleavage [10–12]. However, ithe realization of isoxazoline cycle latent bifunctionality in condensed isoxazolines containing keto group did not give the target acylcyclopentane derivatives, but led to the formation of complex mixture of unidentified products. In this regard, carbonyl group protection as ketal was undertaken for 4-oxocyclopentane[*d*]isoxazolines before the reductive cleavage of isoxazoline cycle.

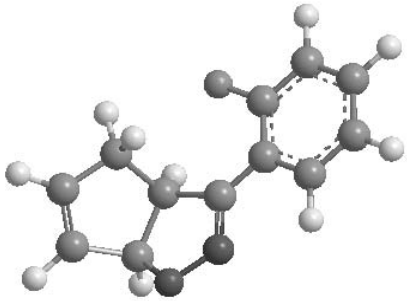


Fig. 2. Ball-and-stick model of 3-(2-fluorophenyl)cyclopent-5-en[*d*]isoxazoline

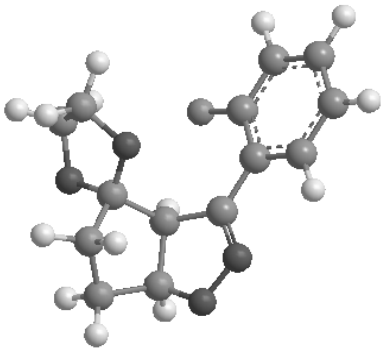
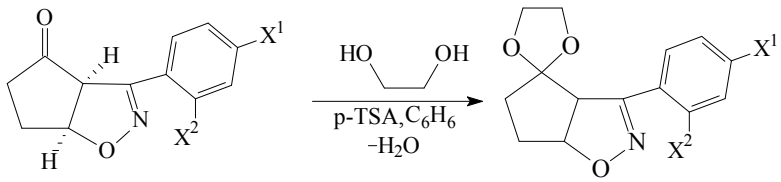


Fig. 3. Ball-and-stick model of 3-(2-fluorophenyl)-4,4-ethylenedioxycyclopenta[*d*]isoxazoline

Reaction of ketone with ethylene glycol in the presence of *n*-toluenesulfonic acid was carried out in a flask fitted with a Dean - Stark trap and reflux condenser to remove water released in the course of the reaction in order to accomplish the equilibrium shift (Scheme 3). The synthesis was terminated when water stopped to gather in the trap. Following aqueous treatment and column chromatography gave the corresponding ethylene ketals **6** along with the conversion of unreacted ketone **5**, the products yields being from moderate to good (Table). Thus, for the reaction of 3-(*n*-fluorophenyl)-4-oxocyclopentane[*d*]-isoxazoline, the product was obtained as crystals with 50.5% yield. The corresponding ethylene ketal was preparared from 3-(*o*-fluorophenyl)-4oxocyclopentane[*d*]isoxazoline with 30.0% yield (Table).



5 **6**

(**а**) X^1 = H, X^2 = F;
(**б**) X^1 = F, X^2 = H

Scheme 3

The structure of the obtained products was confirmed by means of ^{1}H NMR and ^{13}C NMR spectroscopy.

Proton signals of the ethylene ketal group which are chemically nonequivalent for the compounds with substituted aromatic radicals appear in the ^{1}H NMR spectrum of the product **6a** (Fig. 4).

Isoxazoline H-8 and H-12 protons of ketal **6a** (Fig. 4) are observed as doublet of doublets at 4.10 and 5.26 ppm, respectively, whereas in the initial ketone these are observed at 4.34 and 5.56 ppm region, i.e. the two signals are shifted to a stronger field compared with the position of these protons signals in ^{1}H NMR spectrum of the ketone.

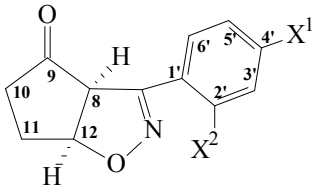
Interestingly, that all protons of cyclopentane ring appear as separate signals in the 3-(2-fluorophenyl)-4.4-ethylenedioxy-cyclopentane-[*d*]isoxazoline ^{1}H NMR spectrum (Fig. 4). Complete assignment of these signals has been proved with the help of double resonance experiments. Thus, the suppression of H-12 signal at 5.26 ppm region as well as that of H-11 at 2.00–2.09 ppm region caused simplification of the H-8 signal which from a doublet of doublets transformed to a doublet with SSCC 2.7 Hz. Furthemore, by suppression of the H-11 signal (2.00–2.09 ppm) the H-12 signal was transformed to a doublet with J = 9.1 Hz which corresponds to its SSC with the H-8 and is characteristic for the relative *cis*-location of these protons. The multiplicity of other protons at C-10 and C-11 positions also changed. Thus, the signal at 1.76 ppm region from a doublet of doublets became a doublet with J = 11.7 Hz, i.e. SSCC equal to 6.7 Hz disappeared, and this couldn't correlated with the C-11 protons geminal constant. Consequently, this signal corresponds to one of the protons at C-10.

Thus, the complete assignment of all signals in the ^{1}H NMR spectrum to all protons present in proposed structural formula of ketal **6a** has been accomplished.

Similar signals are observed in the ^{1}H NMR spectrum of 3-(4-flurophenyl)-4.4-ethylenedioxy-cyclopentane[*d*]isoxazoline, while the H-8 signal (3.99 ppm) shifts to a stronger field by 0.11 ppm compared with *o*-isomer (4.10 ppm). Obviously this is due to a more significant discreening influence on the H-8 chemical shift of fluorine atom as an electron-acceptor substituent in the *o*-position rather than in the *n*-position of the benzene ring of the molecule.

Experimental part. ^{1}H and ^{13}C NMR spectra of substances solutions in $CDCl_3$ containing HMDS as an internal standard have been recorded with Bruker AVANCE spectrometer (400 MHz). The reaction courses was monitored by thin-layer chromatography (TLC) on silica gel plates Kieselgel 60 F_{254} (Merck), the eluent being ether – light petroleum, developer: iodine or 4% $KMnO_4$ solution. The used solvents were purified according to standard procedures [13].

The following atom numeration was used for discussion of spectral data:



2-fluoro- and 4-fluorobenzaldehyde synthesis. 10.1 g (0.15 mol) of hydroxylamine hydrochloride solution in water (30 ml) was added to a stirred solution of 4-flurobenzaldehyde (15.0 g, 0.120 mol) in ethanol (30 ml) with cooling. Then 60 g of ice and 6.0 g (0.15 mol) of sodium hydroxide were added to the reaction mixture. The temperature of the reaction mixture was raised to ambient temperature and the mixture being stirred for additional 4 hours. Then solvent was removed on a rotary evaporator, the residue was extracted with ether (3x30 ml). The combined organic layers were dried on anhydrous sodium sulfate. After separation of the drying agent ether was evaporated on the rotary evaporator. The precipitated crystals were filtered and washed with water.

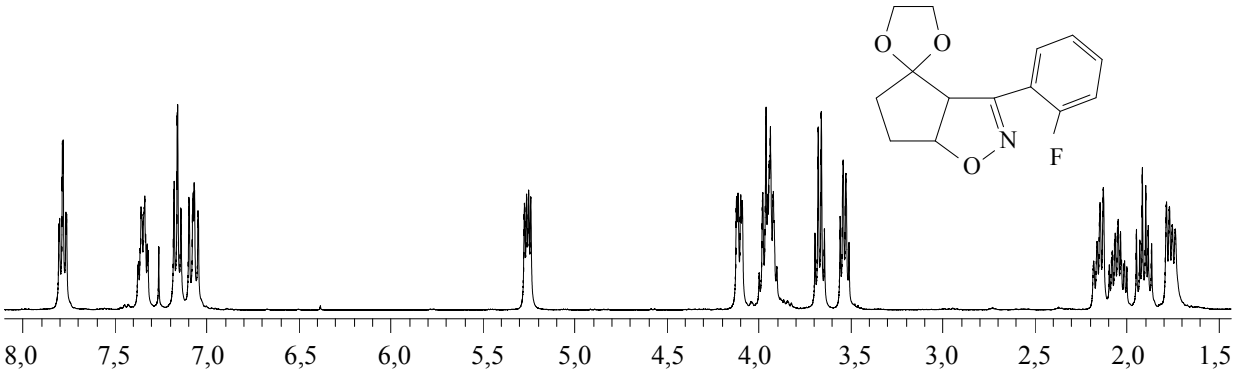


Fig. 4. PMR spectrum of 3-(2fluorophenyl)-4.4-ethylenedioxycyclopent[*d*]isoxazoline

Thus oxime of 4-fluorobenzaldehyde (15.22 g, 91%) was obtained. M.p. 87–90 °C.

Similarly, from 2-fluorobenzaldehyde (15.0 g) oxime of 2-fluorobenzaldehyde (14.84 g, 89%) was obtained, M.p. 69–71 °C.

Synthesis of 2-fluoro and 4-fluoro-N-hydroxibenzimidoyl chlorides. N-chlorosuccinimide (9.75 g (0.073 mol) was added in small portions to a stirred solution of the corresponding aldoxime (10 g, 0.073 mol) in freshly distilled chloroform (155 ml) at room temperature. The reaction proceeded during 24 hours at ambient temperature, and for 2 more hours – at 50 °C. The course of the reaction was monitored by thin layer chromatography.

Then water (20 ml) was added to reaction mixture followed by separation of the organic layer which was dried over anhydrous sodium sulfate. The evaporation of solvent on a rotary evaporator under reduced pressure gave corresponding 2-fluorophenyl- or 4-fluorophenyl- derivatives, the yield being 13.24 g or 16.15 g, respectively. According to TLC the products were clean enough for further use.

Synthesis of 3-aryl-4-oxocyclopentane[*d*]-isoxazolines. Solutions of triethylamine (8.6 ml, 0.062 mol) in ether (30 ml) and of the corresponding hydroximoyl chloride (10.69 g, 0.062 mol) in ether (30 ml) were added simultaneously dropwise from two dropping funnels to a stirred solution of cyclopent-2-enone (5.1 g, 0.062 mol) in of diethyl ether (30 ml). The reaction mixture was stirred at room temperature until disappearance of hydroximoyl chloride (TLC analysis). Then the precipitate was filtered out and washed with diethyl ether. Ether filtrate was removed under reduced pressure. The product was isolated from the resulted residue by column chromatography on silica gel using eluent with gradually increasing polarity (ether – hexane).

4-oxo-3-(2fluorophenyl)cyclopent-[*d*]isoxazoline was obtained as crystals (58.1% yield). M.p. 84–87 °C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.77 dt (1H, H_{ar}-6'; J_1 = 7.4; J_2 = 1.5); 7.37–7.42 m (1H; H_{ar}-4'; J_1 = 7.9; J_2 = 5.1), 7.10–7.20 m (2H; H_{ar}-3'+ H_{ar}-5'; *J* = 7.7); 5,56 dd (1H, H-12 J_1 = 8.7; J_2 = 5.2); 4.34 q (1H, H-8; *J* = 8.7); 2.40–2.54 m (2H, H^A-10 + H^A-11; J_1 = 9.1; J_2 = 5.3); 2.30–2.41 m (2H, H^B-10 + H^B -11, J_1 = 6.8; J_2 = 5.9; J_3 = 2.3).

^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 209.91 (C = O); 160.33 (*J* = 255; C–F); 150.17 (*J* = 4; C=N); 131.91 (*J* = 9; C-4'); 130.02 (*J* = 3, C-6'); 124.20 (*J* = 4; C-5'); 116.42 (*J* = 22; C-3'); 115,92 (*J* = 12; C-1'), 85.61 (C-12); 60,83 (*J* = 4, C-8), 35.29 (C-10), 27.60 (C-11).

4-oxo-3(4-fluorophenyl)-cyclopent[*d*]-isoxazoline was obtained as crystals (40.0% yield). M.p. = = 134–137 °C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.83 m (2H; H_{ar}-2'+ H_{ar}-6'; *J* = 8.8); 7.05 m (2H; H_{ar}-3'+ H_{ar}-5'; *J* = 8.8); 5.52 dd (1H, H-12, J_1 = 8.6; J_2 = 5.1); 4.08 q (1H, H-8; *J* = 8.6); 2.44–2.56 m (2H, H^A-10 + H^A-11; J_1 = 9.0; J_2 = 3.3); 2.30–2.40 m (1H, H^B -11, *J* = 8.4); 2.21–2.28 m (1H, H^B-10; J_1 = 5.4; J_2 = 4.1).

^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 210.18 (C = O); 163.66 (*J* = 255; C–F); 152.17 (C = N); 129.59 (*J* = 8; C-2'+ C-6'); 124,23 (*J* = 4, C-1'); 115.59 (*J* = 22; C-3' + C-5 ') , 85.97 (C-12), 60.04 (C-8), 35.30 (C-10), 27.57 (C-11).

Ethyleneketal protection of 3-aryl-substituted 4-oxocyclopent[*d*]isoxazolines. A mixture consisting from 3-aryl-substituted 4-oxocyclopent[*d*]isoxazoline (2.06 g , 9.4 mmol), of freshly distilled ethyleneglycol (97 ml), of benzene (171 ml) and catalytic amount of *n*-toluene sulphonic acid was refluxed using Dean-Stark trap until water stopped to gather in the trap. Then water was separated, the activated molecular sieves were added into Dean - Stark trap and the reaction mixture was keeping to reflux for additional 3 days. After these the reaction mixture was washed with brine. The organic layer was separated and the aqueous one was extracted with benzene (5 x 50 ml). The combined organic layers were dried over anhydrous sodium sulphate, the solvent was removed on rotary evaporator. The obtained oily crude product was purified by column chromatography on silica gel (eluent: ether – hexane).

3-(2-fluorophenyl)-4.4-ethylenedioxy-cyclopenta[*d*]isoxazoline was obtained as crystals (30.0% yield). M.p. 114–117 °C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.78 gm (1H; H_{ar}-6'; J_1 = 7.7; J_2 = 1.8); 7.35 m (1H, H_{ar}-4'; J_1 = 7.3; J_2 = 1.8); 7.16 gm (1H, H_{ar}-5'; J_1 = 7.6; J_2 = 1.0); 7.07 m (1H; H_{ar}-3'; J_1 = 8.3; J_2 = 1.0); 5.26 dd (1H, H-12, J_1 = 9.1; J_2 = 4.7); 4.10 dd (1H, H-8, J_1 = 9.1; J_2 = 3.2); 3.90–4.00 m (2H, $H_{etilenket}$), 3.67 m (1H, $H_{etilenket}$; *J* = 6.8); 3.54 m (1H, $H_{etilenket}$; J_1 = 6.8); 2,15 dd (1H, H^A-11; J_1 = 13.8; J_2 = 7.3); 2,00–2,09 m (1H, H^B-11; J_1 = 13.8; J_2 = 6.5; J_3 = 4.8); 1.90 td (1H, H^A-10; J_1 = 12.8; J_2 = 7.4); 1.76 dd (1H, H^B-10; J_1 = 12.8; J_2 = 6.7).

^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 159.93 (*J* = 255; C–F); 152.85 (*J* = 2; C=N); 130.86 (*J* = 9; C-4'); 129.43 (*J* = 4, C-6'); 124.30 (*J* = 3; C-5'); 118.80 (*J* = 12; C-1'); 118.48 (C-9); 115.66 (*J* = 22; C-3'), 86.70 (C-12), 64.29 + 65.24 ($C_{etilenket}$); 60.08 (*J* = 6; C-8), 33.02 (C-10), 30.56 (C-11).

3-(4-fluorophenyl)-4.4-ethylenedioxy-cyclopenta[*d*]isoxazoline was obtained as crystals (50.5% yield). M.p. = 115–118°C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.65 m (2H; H_{ar}-2'+ H_{ar}-6'; J_1 = 9.0; J_2 = 5.4; J_3 = 2.1), 7.05 td (2H, H_{ar}-3'+ H_{ar}-5'; J_1 = 9.0; J_2 = 2.1);

5.24 m (1H, H-12, J_1 = 9.0; J_2 = 6.8; J_3 = 4.7; J_4 = 1.9); 3,99 m (1H, $H_{etilenket}$, J = 6.5); 3.87–3.94 m (2H, H-8 + $H_{etilenket}$; J_1 = 9.2; J_2 = 6.7; J_3 = 1.5); 3.74 m (1H, $H_{etilenket}$; J_1 = 13.4; J_2 = 7.5; J_3 = 6.5); 3.58 m (1H, $H_{etilenket}$; J_1 = 14.2; J_2 = 7.5; J_3 = 6.5); 2.04–2.18 m (2H; H^A-11 + H^B-11; J_1 = 13.9; J_2 = 6.7; J_3 = 4.9); 1.86–1.94 m (1H, H^A-10; J_1 = 12.8; J_2 = 10.5; J_3 = 7.6); 1.76–1.82 m (1H, H^B-10; J_1 = 12.8; J_2 = 10.5; J_3 = 6.1).

^{13}C NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 163.24 (J = 255; C–F), 155.15 (C = N), 128.91 (J = 9, C-2'+ + C-6'), 126.62 (J = 4, C-1'), 118.29 (C-9), 115.31 (J = 22, C-3'+ C-5'), 86.92 (C-12), 60.37 + 64.91 ($C_{etilenket}$), 59.31 (C-8), 33.66 (C-10), 30.23 (C-11).

Conclusion. The isoxazolines synthesis has been shown to proceeded with high regio- and stereoselectivity.

The transformation of the prepared isoxazolines into fluorine containing cyclic β-triketones analogues is possible by reductive cleavage of the isoxazoline heterocycle.

The synthesized compounds are precursors of fluorine containing triacylmethane analogues as well as a convenient intermediates in the synthesis of fluorinated prostanoids and other complex natural compounds and their bioactive analogues.

References

1. Исакова, В. Г. Химия фторзамещенных β-дикетонов и их производных / В. Г. Исакова, Т. С. Хлебникова, Ф. А. Лахвич // Ус-пехи химии. – 2010. – Т. 79, № 10. – С. 929–960.

2. Synthesis and properties of fluorinated 2-benzoylcyclohexane-1,3-diones / T. S. Khlebnikova [et al.] // Russian Journal of General Chemistry. – 2007. – Vol. 77, No. 10. – P. 1724–1731.

3. 2-perfluoroalkanoylcyclopentane-1,3-diones. Synthesis and some transformations / T. S. Khlebnikova [et al.] // Russian Journal of Organic Chemistry. – 2012. – Vol. 48, No. 10. – P. 1277–1282.

4. Be´gue´, J.-P. Recent advances (1995–2005) in fluorinated pharmaceuticals based on natural products / J.-P. Be´gue´, D. Bonnet-Delpon // Journal of Fluorine Chemistry. – 2006. – Vol. 127. – P. 992–1012.

5. Isanbor, C. Fluorine in medicinal chemistry: A review of anti-cancer agents / C. Isanbor, D. O'Hagan // Journal of Fluorine Chemistry. – 2006. – Vol. 127. – P. 303–319.

6. Shah, P. The role of fluorine in medicinal chemistry / P. Shah, A. D. Westwell // Journal of Enzyme Inhibition and Medicinal Chemistry. – 2007. – Vol. 22, No. 5. – P. 527–540.

7. Kirsch, K. Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Application. / K. Kirsch. – Weiheim: Willey-VCH, 2004. – 320 p.

8. Barnette, W. E. The synthesis and biology of fluorinated prostacyclins / W. E. Barnette // CRC Crit. Rev. Biochem. – 1984. – Vol. 15, No. 3. – P. 201–235.

9. Серков, И. В. Фторангидриды простагландинов в синтезе производных природных простагландинов по карбоксильной группе / И. В. Серков, В. В. Безуглов // Биоорг. химия. – 2009. – Т. 35, № 1. – С. 122–128.

10. Антоневич, И. П. Взаимодействие 3-фенилциклопентеноизоксазолина с никелем Ренея в трифторуксусной кислоте / И. П. Антоневич, Я. М. Каток, С. В. Нестерова // Труды БГТУ. Сер. IV. Химия и технология орган. в-в. – 2008. – Вып. XVI. – С. 8–11.

11. Антоневич, И. П. Восстановительное расщепление 5-бром-6-гидроксициклопентано-изоксазолинов / И. П. Антоневич, С. В. Нестерова, Я. М. Каток // Труды БГТУ. Сер. IV. Химия и технология орган. в-в. – 2010. – Вып. XVIII. – С. 17–22.

12. Антоневич, И. П. Каталитическое гидрирование ряда 3-арил- и 3-алкилциклопентеноизоксазолинов / И. П. Антоневич, С. В. Нестерова // Труды БГТУ. Сер. IV. Химия и технология орган. в-в. – 2009. – Вып. XVII. – С. 18–22.

13. Armarego, W. L. F. Purification of laboratory chemicals / W. L. F. Armarego, C. L. L. Chai. – 5-th ed. – Oxford: Butterworth – Heinemann, 2003. – 609 p.

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