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RESEARCH ARTICLE

Heterogeneous catalytic reduction of substituted 5-acyl-1,3-dioxanes

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Abstract

Objectives. *To study the hydrogenation of substituted 5-acyl-1,3-dioxanes in the presence of metal-containing catalysts (Pt/Re, Pd/C, Ni/kieselguhr, and Ni/Mo).*
Methods. *In order to determine the qualitative and quantitative composition of the reaction masses, the following analysis methods were used: gas-liquid chromatography (using the Kristall 2000 hardware complex); mass-spectroscopy (using Chromatec-Kristall 5000M device with NIST 2012); nuclear magnetic resonance (NMR) spectrometry (using Bruker AM-500 device with operating frequencies of 500 and 125 MHz).*
Results. *Hydrogenation of substituted 5-acyl-1,3-dioxanes obtained by condensation of carbonyl compounds with paraformaldehyde and sulfuric acid was used to synthesize heterocyclic alcohols in the presence of metal-containing catalysts with a conversion of the initial ketones of 60–90% and a formation selectivity of target products of 70–90%. Substances were analyzed and confirmed by gas-liquid chromatography, mass spectrometry and NMR spectroscopy.*
Conclusions. *The best catalyst for the reduction of substituted 5-acyl-1,3-dioxanes is Pd/C. By using this catalyst, it is possible to achieve a high selectivity for the formation of the corresponding heterocyclic alcohols at a conversion rate of the initial ketones of 60–90%.*

Keywords: *hydrogenation, 5-acyl-1,3-dioxanes, heterocyclic alcohols, catalysts Pt/Re, Pd/C, Ni/kieselguhr, Ni/Mo*

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НАУЧНАЯ СТАТЬЯ

Гетерогенно-каталитическое восстановление замещенных 5-ацил-1,3-диоксанов

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Аннотация

Цели. *Изучить гидрирование замещенных 5-ацил-1,3-диоксанов в присутствии металлосодержащих катализаторов (Pt/Re, Pd/C, «Ni на кизельгуре», Ni/Mo).*
Методы. *Для определения качественного и количественного состава реакционных масс были использованы следующие методы анализа: газожидкостная хроматография (на аппаратно-программном комплексе «Кристалл 2000»), масс-спектроскопия (на приборе «Хроматэк-Кристалл 5000М» с базой NIST 2012), и спектроскопия ядерного магнитного резонанса (ЯМР-спектроскопия) (на приборе «BrukerAM-500» с рабочими частотами 500 и 125 МГц).*
Результаты. *Гидрированием замещенных 5-ацил-1,3-диоксанов, полученных конденсацией карбонильных соединений с параформом с использованием серной кислоты, синтезированы гетероциклические спирты в присутствии металлосодержащих катализаторов с конверсией исходных кетонов 60–90% и селективностью образования целевых продуктов 70–90%. Вещества проанализированы и доказаны методами газожидкостной хроматографии, масс-спектрометрии и ЯМР-спектроскопии.*
Выводы. *Установлено, что лучшим катализатором восстановления замещенных 5-ацил-1,3-диоксанов является Pd/C, позволяющий достичь высокой селективности образования соответствующих гетероциклических спиртов при конверсии исходных кетонов 60–90%.*

Ключевые слова: *гидрирование, 5-ацил-1,3-диоксаны, гетероциклические спирты катализаторы Pt/Re, Pd/C, «Ni на кизельгуре», Ni/Mo*

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INTRODUCTION

Oxymethyl-1,3-dioxacycloalkanes and their derivatives, ethers, esters, thioethers, etc., which exhibit various biologically active properties, are used as corrosion inhibitors, plant protection chemicals [1–3].

The primary method for obtaining alcohols containing a cycloacetal fragment involves the condensation of 1,1,1-trioxymethylalkanes with carbonyl compounds [4, 5]. However, in a number of cases, the use of secondary 1,3-dioxacycloalkane alcohols becomes necessary. Although it has been proposed that these can be obtained by reduction of the keto group in 5-acyl-1,3-dioxanes with metal hydrides [6], such a hydrogenation method is of little use for preparative synthesis under industrial conditions.

In this connection, the present work is aimed at studying the heterogeneous catalytic reduction of substituted 5-acyl-1,3-dioxanes in the presence of various metal-containing catalysts (Pd/C, Ni/kieselguhr, Pt/Re, Ni/Mo).

MATERIALS AND METHODS

After analyzing the reaction masses, the mass spectra of the compounds were recorded using the Chromatec-Kristall 5000M hardware-software complex (*Chromatec*, Russia) with the NIST 2012 database (*National Institute of Standards and Technology*, USA). Analysis conditions were as follows: length of capillary quartz column was 30 m, analysis duration was 20 min, ion source temperature was 260°C, transition line temperature was 300°C, scanning range was 30–300 Da, pressure 37–43 was mTorr, carrier gas was helium, and heating rate was 20 deg/min. Mass spectra of the compounds were obtained using the electron impact ionization method. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-500 spectrometer (*Bruker*, USA) with operating frequencies of 500 and 125 MHz, respectively; the solvent was $CDCl_3$. Chemical shifts are given on a scale of δ (ppm) relative to tetramethylsilane as an internal standard. Spin-spin coupling constants (*J*) are given in Hz.

Starting ketones **1**–**5** were obtained according to the previously presented procedure [7].

1-(5-Methyl-1,3-dioxan-5-yl)ethanone **1**. $T_{b.p.}$ = 99–101°C (3 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.92 s (3H, $\underline{CH_3}C$), 2.22 s (3H, $\underline{CH_3}CO$), 3.45 d (2H, 2 $C\underline{CH_2}$, *J* = 11.6), 4.24 d (2H, 2 $C\underline{CH_2}$, *J* = 11.6), 4.70 d (1H, $\underline{CH_a}O$, *J* = 6.1), 4.74 d (1H, $\underline{CH_b}O$, *J* = 6.0). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 18.28 ($\underline{CH_3}C$), 26.96 ($\underline{CH_3}CO$), 51.15 (C), 71.22 (2 CH_2), 94.55 (CH_2O), 208.92 (C=O).

Mass spectrum, *m/z* (I_{rel}, %): 144 (2) [M^+], 114 (30), 84 (10), 72 (40), 69 (50), 57 (30), 43 (100).

1-(5-Ethyl-1,3-dioxan-5-yl)ethanone **2**. $T_{b.p.}$ = 110–112°C (3 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.75 t (3H, $\underline{CH_3}CH_2$, *J* = 7.6), 1.48 q (2H, $CH_3\underline{CH_2}$, *J* = 7.6, 15.3), 2.25 s (3H, $\underline{CH_3}CO$), 3.57 d (2H, 2 $C\underline{CH_2}$, *J* = 11.5), 4.32 d (2H, 2 $C\underline{CH_2}$, *J* = 11.5), 4.68 d (1H, $\underline{CH_a}O$, *J* = 6.0), 4.88 d (1H, $\underline{CH_b}O$, *J* = 5.9). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 7.78 ($\underline{CH_3}CH_2$,), 25.08 ($CH_3\underline{CH_2}$), 26.98 ($\underline{CH_3}CO$), 51.10 (C), 71.95 (2 CH_2), 94.17 (CH_2O), 208.91 (C=O).

Mass spectrum, *m/z* (I_{rel}, %): 158 (1) [M^+], 128 (10), 99 (5), 83 (30), 71 (7), 67 (10), 57 (20), 43 (100).

1-(5-Isopropyl-1,3-dioxan-5-yl)ethanone **3**. $T_{b.p.}$ = 129–131°C (3 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.9 d (3H, $\underline{CH_3}CH$, *J* = 7.0), 1.00 d (3H, $\underline{CH_3}CH$, *J* = 7.0), 1.63 m (2H, $CH_3\underline{CH}$), 2.27 s (3H, $\underline{CH_3}CO$), 3.48 d (2H, 2 $C\underline{CH_2}$, *J* = 11.5), 4.34 d (2H, 2 $C\underline{CH_2}$, *J* = 11.4), 4.62 d (1H, $\underline{CH_a}O$, *J* = 6.0), 4.98 d (1H, $\underline{CH_b}O$, *J* = 6). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 16.02 ($\underline{CH_3}CH$), 26.94 ($\underline{CH_3}CO$), 29.29 ($CH_3\underline{CH}$), 51.18 (C), 71.76 (2 CH_2), 94.12 (CH_2O), 209.93 (C=O).

Mass spectrum, *m/z* (I_{rel}, %): 158 (2) [M^+], 12 (50), 110 (20), 99 (30), 86 (70), 83 (80), 71 (20), 57 (40), 43 (100).

1-(5-Methyl-1,3-dioxan-5-yl)propan-1-one **4**. $T_{b.p.}$ = 129–131°C (3 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.05 t (3H, $\underline{CH_3}CH_2$, *J* = 7.2), 1.33 s (3H, $\underline{CH_3}C$,), 2.25 q (3H, $\underline{CH_2}CH_3$ *J* = 7.5, 12.0), 3.46 d (2H, 2 $C\underline{CH_2}$, *J* = 11.2), 4.32 d (2H, 2 $C\underline{CH_2}$, *J* = 11.0), 4.62 d (1H, $\underline{CH_a}O$, *J* = 6.0), 4.98 d (1H, $\underline{CH_b}O$, *J* = 6.1). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 9.77 ($\underline{CH_3}CH_2$), 16.33 ($\underline{CH_3}C$), 29.94 ($\underline{CH_2}CO$), 51.13 (C), 73.76 (2 CH_2), 94.12 (CH_2O), 209.92 (C=O).

Mass spectrum, *m/z* (I_{rel}, %): 158 (1) [M^+], 110 (25), 99 (60), 86 (30), 83 (40), 71 (20), 57 (40), 43 (100).

(5-Methyl-1,3-dioxan-5-yl)(phenyl)methanone **5**. $T_{b.p.}$ = 156–157°C (1 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.34 s (3H, $\underline{CH_3}$), 3.78 d (2H, 2 $\underline{CH_2}$, *J* = 11.2), 4.44 d (2H, 2 $\underline{CH_2}$, *J* = 11.3), 4.84 d (1H, $\underline{CH_a}O$, *J* = 5.0), 4.98 d (1H, $\underline{CH_b}O$, *J* = 5.2), 7.4–7.8 m (5H, Ph-). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 18.93 ($\underline{CH_3}$), 47.56 (C), 73.34 (2 CH_2), 91.91 (CH_2O), 205.43 (C=O).

Mass spectrum, *m/z* (I_{rel}, %): 206 (1) [M^+], 188 (20), 176 (40), 108 (100), 87 (20), 81 (90), 55 (60).

General method for hydrogenation of ketones 1–5

In order to study the process of hydrogenation of ketones to obtain alcohols, catalytic hydroprocessing systems, which are widely available in the petrochemical industry, are used [8, 9].

The following commercially available catalysts were used: Pd supported on activated carbon, PK-400 catalyst grade with a Pd content of 2 wt % (*Redkinsky catalyst plant*, Russia); Ni/kieselguhr catalyst—basic nickel carbonate on kieselguhr with the addition of graphite (*Sintez-Kaustik*, Russia) with a Ni content of 45 wt %; Pt/Re catalyst supported on alumina, catalyst grade RB-44 U (*Olkat*, Russia) with a Pt content of 0.25 wt % and Re of 0.4 wt %; bifunctional Ni/Mo catalyst supported on alumina, catalyst grade TK-743 (*Haldor Topsoe*, Denmark) with a Ni content of 5 wt % and Mo of 25 wt %).

The used catalytic systems have proven themselves well in the hydrogenation of acetylene and carbonyl compounds impurities, as well as in the process of hydrocracking, etc. [8–14] (Table 1).

For hydrogenation, a Katakon flow catalytic unit (*Katakon*, Russia) was used, comprising a metal reactor with a heating jacket, a burette for feeding raw materials, an automatic pump, and a control unit. Operating parameters of the installation were as follows: volume of the reaction zone was 15 cm^3, temperature range was 50–600°C, pressure was up to 100 atm.

The required catalyst (Pd/C, Ni/kieselguhr, Pt/Re, or Ni/Mo) was loaded into a flow reactor with a volume of 15 cm^3. The catalyst was activated in a stream of nitrogen or hydrogen at 350–450°C. Additionally, while cooling the reactor to 200°C at a rate of 0.27 mL/min, 15 mL of ketone and hydrogen were supplied at a rate of 0.230 mL/min. The pressure was set at 8 atm. The resulting catalyzate was filtered off and evaporated.

Using this hydrogenation method, the following alcohols were obtained:

1-(5-Methyl-1,3-dioxan-5-yl)ethanol **6**. $T_{b.p.}$ = 105–106°C (3 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.83 s (3H, $\underline{CH_3}C$), 1.14 d (3H, $\underline{CH_3}CH_2$, J = 6.5), 2.22 s (3H, $\underline{CH_3}CO$), 3.45 dd (2H, 2 $C\underline{CH_2}$, J = 11.4, 11.5), 3.75 d (1H, $\underline{CH}OH$, J = 11.4), 4.24 dd (2H, 2 $C\underline{CH_2}$, J = 11.6, 11.2), 4.70 d (1H, $\underline{CH_a}O$, J = 6.1), 4.74 d (1H, $\underline{CH_b}O$, J = 6.0). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 14.28 ($\underline{CH_3}C$), 18.47 ($\underline{CH_3}C$), 26.96 ($\underline{CH_3}CO$), 39.66 (C), 69.44 (CH), 71.43 (CCH_2), 71.92 ($C\underline{CH_2}$), 94.55 (CH_2O).

Mass spectrum, m/z (I_{rel}, %): 146 (2) [M^+], 98 (10), 86 (20), 72 (100), 57 (95), 43 (90).

1-(5-Ethyl-1,3-dioxan-5-yl)ethanol **7**. $T_{b.p.}$ = 122–123°C (3 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.8 t (3H, $\underline{CH_3}CH_2$, J = 11.9), 1.15 d (1H, $\underline{CH_3}CH$, J = 6.5), 1.42–1.55 m (2H, $CH_3C\underline{H_2}$), 3.75 dd (2H, 2 $C\underline{CH_2}$, J = 11.7, 11.4), 3.88 d (1H, $\underline{CH}OH$, J = 11.6), 4.08 dd (2H, $C\underline{CH_2}$, J = 6.8, 10.5), 4.75 d (1H, $\underline{CH_a}O$, J = 6), 4.85 d (1H, $\underline{CH_b}O$, J = 6.0). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 8.49 ($\underline{CH_3}CH_2$), 17.49 ($\underline{CH_3}CH$), 26.81 ($CH_3\underline{CH_2}$), 37.74 (C), 68.38 (CHOH), 73.46 ($C\underline{CH_2}$), 74.13 ($C\underline{CH_2}$), 94.05 (CH_2O).

Mass spectrum, m/z (I_{rel}, %): 160 (≤1) [M^+], 98 (10), 86 (60), 72 (100), 57 (95), 43 (90).

1-(5-Isopropyl-1,3-dioxan-5-yl)ethanol **8**. $T_{b.p.}$ = 131–132°C (2 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 0.9 d (3H, $\underline{CH_3}CH$, J = 9.1), 1.00 d (3H, $\underline{CH_3}CH$, J = 7), 1.27 d (1H, $CH_3\underline{CH}$, J = 6.5), 1.73–1.81 m (2H, $CH_3\underline{CH}$), 3.72 dd

Table 1. Physicochemical and textural characteristics of the catalytic systems used

No.	Indicator	Catalyst			
		Pd/C	Ni/kieselguhr	Pt/Re	Ni/Mo
1	Metal content, wt %	2	45	0.25–0.4	5–25
2	Granule size, mm	2.8–5.5	4.0–5.0	1.6	1.5–3.0
3	Bulk density, g/cm^3	0.52–0.6	1.0–1.3	0.69–0.72	0.58–0.65
4	Specific surface area, m^2/g	230	280	170–210	180
5	Metal particle size, nm	1.5–2	6–8	4–6	4–6
6	Pore volume, cm^3/g	0.5	0.6	0.5	0.85–0.96

(2H, C$\underline{CH_2}$, J = 6.0, 11.0), 4.00 d (1H, CHOH, J = 11.6), 4.12 dd (2H, C$\underline{CH_2}$, J = 6.6, 11.5), 4.67 d (1H, $\underline{CH_a}$O, J = 5.8), 4.88 d (1H, $\underline{CH_b}$O, J = 5.8). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 16.02 ($\underline{CH_3}$CH), 19.27 ($CH_3\underline{CH}$), 26.91 ($\underline{CH_3}$CO), 39.17 (C), 68.44 ($\underline{CH}$OH), 72.41 (C$\underline{CH_2}$), 72.66 (C$\underline{CH_2}$), 94.14 (CH_2O).

Mass spectrum, m/z (I_{rel}, %): 160 (2) [M^+], 72 (60), 57 (50), 45 (30), 43 (70), 39 (20), 32 (100).

1-(5-Methyl-1,3-dioxan-5-yl)propan-1-ol **9**. $T_{b.p.}$ = 114–116°C (2 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.02 t (3H, $\underline{CH_3}CH_2$, J = 7.5), 1.33 s (3H, $\underline{CH_3}$C,), 2.12 d (1H, $\underline{CH_a}$, J = 8.0), 2.23 d (1H, $\underline{CH_b}$, J = 8.1). 3.98 d (1H, $\underline{CH}$OH, J = 11.4), 4.32 dd (4H, 2 C$\underline{CH_2}$, J = 11.0, 7.0), 4.77 d (1H, $\underline{CH_a}$O, J = 6.0), 4.94 d (1H, $\underline{CH_b}$O, J = 6.1). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 11.77 ($\underline{CH_3}CH_2$), 16.35 ($\underline{CH_3}$C), 27.93 ($\underline{CH_2}$CO), 39.17 (C), 68.42 ($\underline{CH}$OH), 72.47 (C$\underline{CH_2}$), 74.61 (C$\underline{CH_2}$), 94.12 (CH_2O).

Mass spectrum, m/z (I_{rel}, %): 160 (1) [M^+], 99 (60), 86 (80), 71 (40), 57 (70), 43 (100).

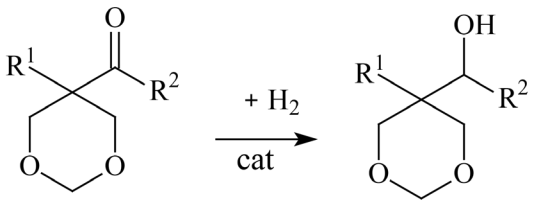
5-Methyl-1,3-dioxan-5-yl-(phenyl)methanone **10**. $T_{b.p.}$ = 163–165°C (1 mm Hg). Colorless liquid. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.06 s (3H, $\underline{CH_3}$), 3.79 dd (2H, C$\underline{CH_2}$, J = 11.7, 11.4), 3.94 d (1H, $\underline{CH}$OH, J = 11.0), 4.08 dd (2H, C$\underline{CH_2}$, J = 6.8, 10.5), 4.88 d (1H, $\underline{CH_a}$O, J = 5.2), 4.92 d (1H, $\underline{CH_b}$O, J = 5.2), 7.2–7.8 m (5H, Ph-). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 18.81 ($\underline{CH_3}$), 39.51 (C), 73.32 (2 CH_2), 75.31 (CH), 91.94 (CH_2O), 129.44–139.22 (Ph-).

Mass spectrum, m/z (I_{rel}, %): 208 (1) [M^+], 108 (100), 104 (60), 87 (20), 55 (60).

RESULTS AND DISCUSSION

Previously [7], we showed that in a hydrogen flow in the presence of a Pd/C catalyst, 5-acyl--1,3-dioxanes are reduced to the corresponding heterocyclic alcohols. Continuing this work, we studied the hydrogenation of heterocyclic ketones **1**–**5** in the presence of a number of industrial metal-containing catalysts: Pd/C, Ni/kieselguhr, Pt/Re, or Ni/Mo.

Among the catalysts studied (Table 2), the best performance was demonstrated by Pd/C, which is used in the reduction of unsaturated and carbonyl compounds [15–19]. The conversion on Pt- and Ni-catalysts was 1.5–2.5 times lower; in all cases, the selectivity was more than 70%.



1–5 **6–10**

$R^1 = CH_3$, $R^2 = CH_3$ (**1**, **6**), $R^1 = C_2H_5$, $R^2 = CH_3$ (**2**, **7**)
$R^1 = i\text{-}C_3H_7$, $R^2 = CH_3$ (**3**, **8**), $R^1 = CH_3$, $R^2 = C_2H_5$ (**4**, **9**)
$R^1 = CH_3$, R^2 = Ph (**5**, **10**)

Scheme 1. Hydrogenation of 5-acyl-1,3-dioxanes.

Table 2. Hydrogenation of substituted 5-acyl-1,3-dioxanes **1**–**5** in the presence of various catalysts. Synthesis conditions: 200°C, reaction time = 1 h, molar ratio of ketone/H_2 = 1 : 6.

Starting compounds	Reaction products	Catalyst							
		Pd/C		Pt/Re		Ni/kieselguhr		Ni/Mo	
		*C**, %	*S**, %	*C*, %	*S*, %	*C*, %	*S*, %	*C*, %	*S*, %
1	**6**	80	98	70	95	50	85	40	95
2	**7**	90	95	50	95	40	80	40	90
3	**8**	80	95	40	95	30	80	20	95
4	**9**	60	95	50	80	30	60	30	80
5	**10**	65	95	40	70	25	75	20	70

Note: *C* is a conversion, %; *S* is a selectivity, %.

The conversion of ketones **1**–**5** is also affected by substituents having different structures at the carbonyl group and the 5th position of the 1,3-dioxane ring. The ethyl and phenyl radicals at the C=O group reduce the conversion of compounds **4** and **5**. The activity of ketones **2** and **3**, containing ethyl or isopropyl groups in the 5th position, slightly decreases as compared to methyl ethyl ketone derivative **1**.

It is noted that the hydrogenation of ketone **5** did not reveal products of complete or partial reduction of the aromatic nucleus.

CONCLUSIONS

The heterogeneous Pd/C catalyst allows 5-acyl-1,3-dioxanes to be reduced to the corresponding alcohols with a selectivity of more than 95%. Ni-containing catalysts are significantly less active when used in this process.

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Authors' contributions

A.I. Musin – conducting research, literature review on the topic of the article;

Yu.G. Borisova – collection and processing of the material, writing the text of the article;

G.Z. Raskil'dina – statistical processing;

A.R. Davletshin – processing of the material;

R.R. Daminev – consultation on planning, methodology, and research implementation;

S.S. Zlotskii – development of the concept of scientific work, critical revision with the introduction of valuable intellectual content.

The authors declare no conflicts of interest.

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