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SYNTHESIS AND CHEMICAL MODIFICATION OF NEW HYDROXYBEZALDEHYDE DERIVATIVES

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Abstract. *Introduction.* A high pharmacological ability of aromatic benzaldehydes makes them important intermediates for the synthesis of medicinal preparations, such as anticancer, bactericidal, antifungal, and herbicidal drugs. *The purpose of this work* is the synthesis of biologically active compounds, based on 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde and the establishment of the structure of the synthesized compounds. *Results and discussion.* New carbonodithioates, based on O-aromatic systems have been synthesized by the interaction of 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde with carbon disulfide in the presence of sodium hydroxide in ethanol at the room temperature. As a result of the reactions, sodium O-(4-formylphenyl)carbodithioate (86 %) and sodium O-(4-formyl-2-methoxyphenyl)carbodithioate (80%) have been isolated. The interaction of sodium xanthates with acid chlorides (4-methoxy-, 4-nitro-, 2,4-dinitrobenzoic) in chloroform has led to the formation of aromatic thioanhydrides of carbonodithioic acids in 55-80 % yields. The reactivity of hydroxybenzaldehydes and their dithiocarboxylic derivatives has been studied in the propargylation reaction. Propargylation of 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde has been carried out with propargyl bromide in the presence of a 3-fold excess of K_2CO_3 in acetone at the temperature of 60°C. The propargylation reaction of sodium xanthate has been carried out with propargyl bromide in acetone at the room temperature. *Conclusion.* As a result of the reactions, carbonodithioates, thioanhydrides, acetylenic and thioacetylenic ethers have been synthesized based, on O-aromatic systems (4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde). The structure of the synthesized compounds has been established on the basis of elemental analysis data, IR spectra, ^1H and ^{13}C NMR spectroscopy.

Key words: sodium xanthates, thioanhydrides, propargylation, acetylenic and thioacetylenic ethers

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1. Introduction

Derivatives of aromatic aldehydes and their analogues are widely used in the food, perfumery and pharmaceutical industries as a denaturant, flavoring agent and perfume [1], in the chemical industry for the production of dyes.

Due to their chemotherapeutic potential and low toxicity, benzaldehyde derivatives exhibit an antitumor activity [2-5]. 3,4-Dihydroxybenzaldehyde protect human blood cells from oxidative damage, caused by Cr(VI), and also improve the antioxidant capacity of erythrocytes and restore the activity of the major antioxidant, metabolic and membrane-bound enzymes [6].

An extract from the medicinal plant *Gastrodia elata*. (Tianma), which contains 4-hydroxybenzaldehyde (4-HBA), is used to treat kidney diseases, neuralgia, and nervous disorders [7]. 4-HBA is an active candidate for improving insulin resistance and cholinesterase inhibition and may become a new therapeutic agent for the treatment of acute wounds [8].

Despite their fungistatic and antibacterial activity, benzaldehyde derivatives also show high activity against pathogenic microorganisms. [9-11].

Thus, the published data on the biological activity of aromatic benzaldehydes and their derivatives allow us to unequivocally conclude that interest in this class of compounds still remains unchanged.

2. Experimental part

The progress of the reactions and the purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates with the display of spots of the compounds with iodine vapor, eluent (H_2O), benzene and acetone/hexane (1/3, 1/1). The IR spectra were recorded on a Nicolet 5700 spectrometer in tablets with KBr. The melting points of the compounds were determined on a Hanon MP450 instrument. The ^{1}H and ^{13}C NMR spectra of the compounds were recorded on a JNM-ECA 400 spectrometer (Jeol) with the operating frequency of 400 (^{1}H) and 100 MHz (^{13}C) of the deuterated DMSO-d_6 solution. The elemental analysis was carried out on a Rapid Micro N Cube elemental analyzer (Elementar, Germany, 2015).

Sodium O-(4-formylphenyl)carbonodithioate (3). To a solution of 3.0 g (0.004 mol) of 4-hydroxybenzaldehyde in 15 ml of alcohol was added a solution of 1.59 g (0.004 mol) of sodium hydroxide in 5 ml of distilled water. Then, a solution of 3.11 g (0.004 mol) of carbon disulfide was added dropwise and stirred at the room temperature. After the complete dropping of carbon disulfide, the reaction mixture was stirred at the room temperature for four hours. The solvent was distilled off in a water-jet pump vacuum, the solid residue was purified by the recrystallization from acetonitrile. Yield 7.75 g (86%), R_f 0.89 (H_2O), m.p. 302°C. Found, %: C 43.79; H 2.37; S 29.28. $C_8H_5NaO_2S_2$. Calculated, %: C 43.63; H 2.29; S 29.12. IR spectra (KBr), ν, cm^{-1}: 1159 (C=S), 611 (C–S), 1678 (C=O) и 3412, 1500, 1303, 1107, 848, 509 (Ph).

Sodium O-(4-formyl-2-methoxyphenyl)carbonodithioate (4) was synthesized in a similar way. Yield 3.40 g (69%), R_f 0.7 (H_2O), m.p. above 350°C. Found, %:

C 43.79; H 2.37; S 29.28. $C_9H_7NaO_3S_2$. Calculated, %: C 43.19; H 2.82; S 25.62. IR spectra (KBr), ν, cm^{-1}: 613 (C–S), 1023 (C=S), 2851 (OCH_3), 1649 (C=O) и 3412, 1501, 1318, 1120, 872, 775 (Ph). NMR ^1H spectra (DMSO-*d_6*), δ, ppm: 3.47 (s, 3H, CH_3); 6.10 (s, 1H, Ph); 6.82 (d, 1H, Ph); 6.95 (d, 1H, Ph); 9.10 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 54.9 (OCH_3); 107.5; 117.7, 118.5, 131.1, 150.5, 151.6 (Ph), 170.4 (C=O); 187.1 (C=S).

4-Methoxybenzoic (O-(4-formyl-2-methoxyphenyl)carbonothioic) thioanhydride (5). A solution of 1.36 g (0.008 mol) of 4-methoxybenzoyl chloride was added dropwise to a solution of 2 g (0.0085 mol) sodium O-(4-formyl-2-methoxyphenyl) carbonodithioate in 25 ml of chloroform with stirring. The mixture was stirred at room temperature of 22 °C for two hours. The solvent was distilled off in a water-jet pump vacuum, the product was isolated by recrystallization from hexane. Yield 2.31 g (80%), R_f 0.88 (acetone/hexane, 1/3), m.p. 122ºC. Found, %: C 56.47; H 3.98; S 17.57. $C_{17}H_{14}O_5S_2$. Calculated, %: C 56.34; H 3.89; S 17.69. IR spectra (KBr), ν, cm^{-1}: 677 (C–S), 1023 (C=S), 1678 (C=O), 2851 (OCH_3). NMR ^1H spectra (DMSO-*d_6*), δ, ppm: 3.74 (s, 6H, OCH_3); 6.85 (s, 1H, Ph); 7.00 (d, 2H, Ph); 7.27 (d, 1H, Ph); 7.52 (d, 1H, Ph); 7.96 (d, 2H, Ph); 9.88 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 56.0, 56.4 (OCH_3); 112.4, 114.7; 120.7, 126.4,129.2, 132.6, 135.5, 152.2, 153.4, 164.3 (Ph), 191.3, 192.4 (C=O); 198.3 (C=S).

4-Nitrobenzoic (O-(4-formyl-2-methoxyphenyl)carbonothioic) thioanhydride (6) was synthesized in a similar way. Yield 1.25 g (55%), m.p. 184ºC. Found, %: C 51.07; H 2.85; N 3.83; S 17.11.$C_{16}H_{11}NO_6S_2$. Calculated, %: C 50.92; H 2.94; N 3.71; S 16.99. IR spectra (KBr), ν, cm^{-1}: 711 (C–S), 1084 (C=S), 1698, 1746 (C=O), 2851 (OCH_3), 3290 (NO_2). NMR ^1H spectra (DMSO-*d_6*), δ, ppm: 3.82 (s, 3H, OCH_3); 7.52 (s, 1H, Ph); 7.61 (d, 1H, Ph); 8.33 (d, 1H, Ph); 9.96 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 56.6 (OCH_3); 112.7, 123.7; 124.6, 131.9, 134.1, 136.0, 144.3, 151.3, 151.9 (Ph), 162.7 (C=O); 192.5 (C=S).

3,5-Dinitrobenzoic (O-(4-formyl-2-methoxyphenyl)carbonothioic) thioanhydride (7) was synthesized in a similar way. Yield 1.64 g (64%), m.p. 129ºC. Found, %: C 45.67; H 2.55; N 6.73; S 15.01.$C_{16}H_{10}N_2O_8S_2$. Calculated, %: C 45.50; H 2.39; N 6.63; S 15.18. IR spectra (KBr), ν, cm^{-1}: 726 (C–S), 1029 (C=S), 1698, 1745 (C=O), 2852 (OCH_3), 3295 (NO_2). NMR ^1H spectra (DMSO-*d_6*), δ, ppm: 3.84 (s, 3H, OCH_3); 7.55-7.63 (m, 3H, Ph); 8.85 (s, 1H, Ph); 9.03 (s,1H, Ph), 9.08 (s, 1H, Ph); 9.97 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 56.7 (OCH_3); 112.8, 123.8; 129.9, 131.6, 136.2, 144.0, 149.1, 151.8 (Ph), 161.0 (C=O); 192.4 (C=S).

3,5-Dinitrobenzoic O-(4-formylphenyl)carbonothioic) thioanhydride (8) was synthesized in a similar way. Yield 2.75 g (77%), R_f 0.89 (acetone/hexane, 1/3), m.p. 145ºC. Found, %: C 46.07; H 2.18; N 7.28; S 16.25.$C_{15}H_8N_2O_7S_2$. Calculated, %: C 45.92; H 2.06; N 7.14; S 16.34. IR spectra (KBr), ν, cm^{-1}: 698 (C–S), 1080 (C=S), 1685, 1747 (C=O), 3287 (NO_2). NMR ^1H spectra (DMSO-d_6), δ, ppm: 7.56 (d, 2H, Ph); 7.99 (d, 2H, Ph); 9.03 (d,1H, Ph), 9.68 (s, 1H, Ph);

9.96 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 116.2, 123.1, 129.9, 131.7, 132.5, 134.9, 148.8, 155.0 (Ph), 161.6, 163.7 (C=O); 192.5 (C=S).

4-(Prop-2-yn-1-yloxy)benzaldehyde (9). To a mixture of 16 g (0.1157 mol) of potash in 50 ml of acetone was added 5.0 g (0.040 mol) of 4-hydroxybenzaldehyde. Then, a solution of 4.7 g (0.040 mol) of propargyl bromide in 10 ml of acetone was added dropwise to the mixture with stirring and heating to 50°C, and the mixture was stirred for 8 h. The reaction mixture was concentrated, and the residue was washed with hexane. Yield 3.6 g (55%), R_f 0.51 (benzene), m.p. 82 °C. Found, %: C 75.09; H 5.15. $C_{10}H_8O_2$. Calculated, %: C 74.99; H 5.03. IR spectra, ν, cm^{-1}: 1678 (C=O), 2121 (C≡C), 3205 (≡C–H). NMR ^{1}H spectra (DMSO-d_6), δ, ppm: 2.55 (t, 1H, ≡CH); 4.67 (s, 2H, OCH_2); 6.99 (d, 2H, Ph); 7.75 (d, 2H, Ph); 9.78 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 56.0 (OCH_2); 76.7, 77.6 (C≡C); 115.1, 130.5, 131.9, 162.3 (Ph), 190.8 (C=O).

3-Methoxy-4-(prop-2-yn-1-yloxy)benzaldehyde (10) was synthesized in a similar way. Yield 3.61 g (58%), R_f 0.72 (acetone/hexane, 1/1), m.p. 86°C. Found, %: C 69.57; H 5.43. $C_{11}H_{10}O_3$. Calculated, %: C 69.46; H 5.30. IR spectra, ν, cm^{-1}: 1685 (C=O), 2125 (C≡C), 3244 (≡CH). NMR ^{1}H spectra (DMSO-d_6), δ, ppm: 2.49 (t, 1H, ≡CH); 3.56 (s, 3H, OCH_3); 4.58 (s, 2H, OCH_2); 6.75 (s, 1H, Ph); 6.87 (d, 1H, Ph); 7.15 (d, 1H, Ph); 9.54 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 56.3 (OCH_3); 57.1 (OCH_2); 76.1, 78.7 (C≡C); 109.3; 112.3; 126.0; 130.5; 149.7; 151.9 (Ph), 190.9 (C=O).

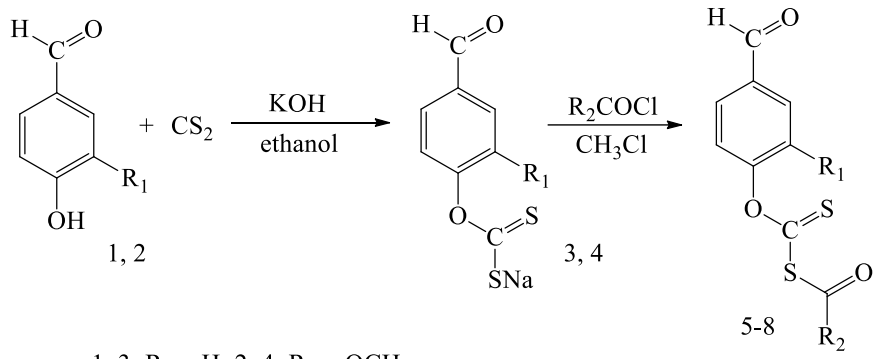
O-(4-Formylphenyl)-S-prop-2-yn-1-yl carbonodithioate (11). A solution of 2.1 g (0.018 mol) of propargyl bromide in 5 ml of acetone was added dropwise to a solution of 4 g (0.018 mol) sodium O-(4-formylphenyl)carbonodithioate in 25 ml of acetone at the temperature of ~20°C and stirred for 4 h. The reaction mixture was concentrated and the residue was washed with hexane. Yield 2.75 g (65%), R_f 0.87 (acetone/hexane, 1/3), m.p. 67.7°C. Found, %: C 56.07; H 3.53; S 27.25. $C_{11}H_8O_2S_2$. Calculated, %: C 55.91; H 3.41; S 27.14. IR spectra (KBr), ν, cm^{-1}: 605 (C−S), 1006 (C=S), 1678 (C=O), 2121 (C≡C), 3205 (≡CH). NMR ^{1}H spectra (DMSO-d_6), δ, ppm: 2.54 (t, 1H, ≡CH); 4.67 (s, 2H, SCH_2); 6.98 (d, 2H, Ph); 7.74 (d, 2H, Ph); 9.77 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 27.4 (SCH_2); 76.7, 78.6 (C≡C); 115.1, 130.5, 131.9, 152.1 (Ph), 162.3 (C=O); 191.0 (C=S).

O-(4-Formyl-2-methoxyphenyl)-S-prop-2-yn-1-yl carbonodithioate (12) was synthesized in a similar way. Yield 3.25 g (76%), R_f 0.85 (acetone/hexane, 1/3). Found, %: C 54.21; H 3.63; S 24.21. $C_{12}H_{10}O_3S_2$. Calculated, %: C 54.12; H 3.78; S 24.08. IR spectra (KBr), ν, cm^{-1}: 655 (C−S), 1029 (C=S), 1666 (C=O), 2120 (C≡C), 3244 (≡CH). NMR ^{1}H spectra (DMSO-d_6), δ, ppm: 2.52 (t, 1H, ≡CH); 3.72 (s, 3H, OCH_3); 4.67 (s, 2H, SCH_2); 6.95 (s, 1H, Ph); 7.19 (d, 1H, Ph); 7.28 (d, 1H, Ph); 9.69 (s, 1H, HCO). NMR ^{13}C spectra (DMSO-d_6), δ, ppm: 27.5 (SCH_2); 56.0 (OCH_3); 76.2, 78.7 (C≡C); 111.3; 112.3; 126.1; 130.7; 149.8; 152.0 (Ph), 162.2 (C=O); 190.9 (C=S).

3. Results and discussion

In order to synthesize new biologically active substances among the organosulfur compounds, the conditions for the synthesis of aromatic benzaldehyde xanthogenates and their derivatives: thioanhydrides and thioacetylene ethers have been developed. Benzaldehydes: 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde have been taken as initial substrates.

The reaction of the interaction of equimolar amounts of benzaldehydes (4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde) with carbon disulfide has been carried out in the presence of sodium hydroxide in ethanol at the temperature of 22°C. The isolation of the synthesized xanthates from the reaction mixture has been carried out by the recrystallization from acetonitrile. As a result, sodium O-(4-formylphenyl)carbonodithioate 3 and sodium O-(4-formyl-2-methoxyphenyl)carbonodithioate 4 have been synthesized in 86 and 80% yield, respectively.



1, 3: R_1 = H; 2, 4: R_1 = OCH_3.

5: R_1 = OCH_3; R_2 = 4-MetC_6H_4; 6: R_1 = OCH_3; R_2 = 4-$NO_2C_6H_4$;

7: R_1 = OCH_3; R_2 = 2,4-$(NO_2)_2C_6H_3$; 8: R_1 = H; R_2 = 2,4-$(NO_2)_2C_6H_3$.

Acylation of xanthates has been carried out by the interaction of sodium O-(4-formylphenyl)carbonodithioate 3 and sodium O-(4-formyl-2-methoxyphenyl)carbonodithioate 4 with acid chlorides (4-methoxy-, 4-nitro-, 2,4-dinitrobenzoic) in chloroform at the temperature of 25°C for 3 hours. As a result of the isolation from the reaction mixtures, thioanhydrides 5-8 have been obtained individually in 55-80% yields, respectively.

The composition and identity of the synthesized compounds 3-8 have been confirmed by the elemental analysis, TLC, IR-, ^{1}H and ^{13}C NMR spectroscopy.

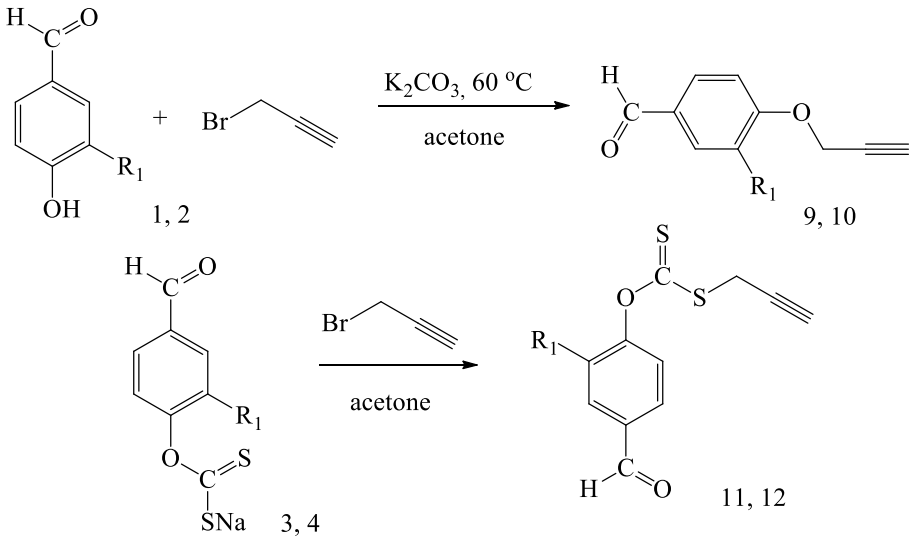
In the IR spectra of compounds 5-8, absorption bands of stretching vibrations of the C=S group are observed in the region of 1029-1084 cm^{-1}. Stretching vibrations of the C-S bond are present in the region of 677-726 cm^{-1}. As well as the presence of intense absorption bands of the C=O group in the region of 1678-1747 cm^{-1}.

In the ^{1}H NMR spectra of thioanhydrides 5-8, protons of the phenyl groups are located in the low field region at δ 6.85-9.68 ppm. The aldehyde proton appeared as a one-proton singlet at δ 9.88-9.97 ppm. The protons of the -OCH_3 methoxy group of compounds 5-7 have appeared as a singlet in the region of δ 3.74-3.84 ppm.

The ^{13}C NMR spectrum data also confirm the structure of compounds 5-8. The signals of the carbon atom of the C=O and C=S groups appear in the low field region δ 161.0-192.4 ppm and 192.5-198.3 ppm.

In order to study the reactivity of benzaldehydes and their dithiocarbamine derivatives, as well as the synthesis of thioacetylenic ethers, the propargylation reaction of 4-hydroxybenzaldehyde 1 and 4-hydroxy-3-methoxybenzaldehyde 2, sodium O-(4-formylphenyl)carbonodithioate 3 and sodium O-(4-formyl-2-methoxyphenyl) carbonodithioate 4 has been investigated.

The synthesis has been carried out by the interaction of 4-hydroxybenzaldehyde 1 and 4-hydroxy-3-methoxybenzaldehyde 2 with propargyl bromide in the presence of a threefold excess of K_2CO_3 in acetone at the temperature of 60°C. Whereas the propargylation of xanthates sodium O-(4-formylphenyl)carbonodithioate 3 and sodium O-(4-formyl-2-methoxyphenyl)carbonodithioate 4 has been carried out at the room temperature.



1, 3, 9, 11: R_1 = H; 2, 4, 10, 12: R_1 = OCH_3.

After processing the reaction mixtures, acetylenic and thioacetylenic derivatives 9-12 have been isolated with the corresponding yields of 59-90 %.

The structure of the synthesized compounds 9-12 has been established, based on the IR, ^{1}H and ^{13}C NMR spectroscopy data.

The IR spectra of compounds 9-12 show the absorption bands of stretching vibrations of C≡CH bond in the region of 3205-3244 cm^{-1} and C≡C bond in the region of 2120-2125 cm^{-1}. There are intense absorption bands of the C=S group in the region of 1006 and 1029 cm^{-1}, as well as stretching vibrations of the C-S bond in the region of 605 and 655 cm^{-1} in the IR spectra of compounds 9, 10.

The ^{1}H NMR spectra of the compounds 9-12 have contained the following characteristic signals: triplet of acetylene proton at δ 2.49-2.55 ppm, doublet of protons of the O-methylene (S-methylene) groups at δ 4.67 and 4.58 ppm (δ 4.67 ppm). The chemical shifts of the protons of the Ph group are located in the weak field region at δ 6.75-7.75 ppm. The mobile hydrogen atom at the aldehyde group appears in the weak field region at δ 9.54-9.78 ppm. The ^{1}H NMR of compounds 10, 12 have contained the resonance signal of the methoxy group in a singlet at δ 3.72 and 3.56 ppm corresponding to three protons.

The ^{13}C NMR spectrums of the compounds 9-12 have the following characteristic chemical shifts: signals of O-methylene carbon atoms appear at δ 56.0 and 57.1 ppm and S-methylene carbon atoms at δ 27.4 and 23.5 ppm, acetylene carbon atoms give resonance signals at δ 76.1-76.7 ppm and 77.6-78.7 ppm. In the ^{13}C NMR spectrums of the compounds 10 and 12, the signals of the methoxy carbon atom are observed at δ 56.3 and 56.0 ppm. The signals of the aromatic carbon atoms are located in the downfield part of the spectrum at δ 109.3-162.3 ppm. The signal of the carbon atom of the C=O group appears in the low field region at δ 162.3-190.9 ppm. In the ^{13}C NMR spectra of the compounds 11 and 12, the carbon atom of the C=S bond resonates as a singlet in the region of δ 191.0 and 190.9 ppm.

4. Conclusion

New 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde derivatives: carbonodithioates, thioanhydrides, acetylenic and thioacetylenic ethers have been synthesized. Aromatic thioanhydrides of carbonodithioic acids have been synthesized by the reaction of acylation of hydroxybenzaldehyde xanthates. The propargylation reaction of benzaldehydes and their sodium xanthates has been studied. It has been established that the propargylation of sodium O-(4-formylphenyl)carbonodithioate and sodium O-(4-formyl-2-methoxyphenyl)carbonodithioate proceeds more easily and in higher yields as compared with the initial hydroxybenzaldehydes.

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Conflict of Interest: All authors declare that they have no conflict of interest.

ГИДРОКСИБЕЗАЛЬДЕГИДТІҢ ЖАҢА ТУЫНДЫЛАРЫН СИНТЕЗДЕУ ЖӘНЕ ХИМИЯЛЫҚ ТҮРЛЕНДІРУ

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Түйіндеме. *Кіріспе.* Ароматикалық бензальдегидтердің жоғары фармакологиялық қасиеті оларды қатерлі ісікке қарсы, бактерицидтік, саңырауқұлаққа қарсы және гербицидтік препараттар сияқты дәрілік заттарды синтездеу үшін маңызды интермедиаттарға айналдырады. Жұмыстың *мақсаты* 4-гидроксибензальдегид пен 4-гидрокси-3-метоксибензальдегид негізінде биологиялық белсенді қосылыстарды синтездеу және синтезделген қосылыстардың құрылымын анықтау. *Нәтижелер және талқылау.* Жаңа карбонодитиоат о-ароматты жүйелер негізінде, бөлме температурасында этанол ортасында натрий гидроксиді қатысында 4-гидроксибензальдегид пен 4-гидрокси-3-метоксибензальдегидтің күкіртті көміртегімен әрекеттесуі арқылы синтезделеді. Реакция нәтижесінде натрий О-(4-формилфенил) карбодитиоаты (86%) және натрий О-(4-формил-2-метоксифенил) карбодитиоаты (80%) бөлініп алынды. Хлороформ ортасында натрий ксантогенаттарының хлорангидридтермен (4-метокси-, 4-нитро-, 2,4-динитробензой) өзара әрекеттесуі 55-80% өнімділікпен карбонодитио қышқылдарының ароматикалық тиоангидридтерінің түзілуіне әкелді. Гидроксибензальдегидтердің және олардың дитиокарбон туындыларының пропаргилдеу реакциясындағы реактивтілік қабілеті зерттелді. 4-гидроксибензальдегидті, 4-гидрокси-3-метоксибензальдегидті пропаргилдеу 60 °С температурада ацетон ортасында K_2CO_3 3 есе артық қатысуымен бромды пропаргилмен жүргізілді. Натрий ксантогенаттарының пропаргилдеу реакциясы бөлме температурасында ацетон ортасында бромды пропаргилмен жүргізілді. *Қорытынды.* Реакция нәтижесінде О-ароматты жүйелер (4-гидроксибензальдегид және 4-гидрокси-3-метоксибензальдегид) негізінде карбонодитиоаттар, тиоангидридтер, ацетилен және тиоацетилен эфирлері синтезделді. Синтезделген қосылыстардың құрылымы элементтік талдау, ИҚ спектрлері, ^{1}Н және ^{13}С ЯМР спектроскопиясы негізінде анықталды.

Түйін сөздер: натрий ксантогенаты, тиоангидридтер, пропаргилдеу, ацетиленді және тиоацетиленді эфирлер

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СИНТЕЗ И ХИМИЧЕСКАЯ МОДИФИКАЦИЯ НОВЫХ ПРОИЗВОДНЫХ ГИДРОКСИБЕНЗАЛЬДЕГИДОВ

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Резюме. *Введение.* Высокая фармакологическая способность ароматических бензальдегидов делает их важными интермедиатами для синтеза лекарственных средств, например, противораковых, бактерицидных, противогрибковых и гербицидных препаратов. *Целью данной работы* является синтез биологически активных соединений на основе 4-гидроксибензальдегида и 4-гидрокси-3-метоксибензальдегида, и установление строения синтезированных соединений. *Результаты и обсуждение.* Синтезированы новые карбонодитиоаты на основе О-ароматических системах, взаимодействием 4-гидроксибензальдегида и 4-гидрокси-3-метоксибензальдегида с сероуглеродом в присутствии гидроксида натрия в среде этанола при комнатной температуре. В результате реакций выделены О-(4-формилфенил)карбодитиоат натрия (86%) и О-(4-формил-2-

метоксифенил)карбодитиоат натрия (80%). Взаимодействие ксантогенатов натрия с хлорангидридами (4-метокси-, 4-нитро-, 2,4-динитробензойный) в среде хлороформа приводило к образованию ароматических тиоангидридов карбонодитиоевых кислот с выходами 55-80%. Изучена реакционная способность гидроксибензальдегидов и их дитиокарбоновых производных в реакции пропаргилирования. Пропаргилирование 4-гидроксибензальдегида, 4-гидрокси-3-метоксибензальдегида проводили бромистым пропаргилом в присутствии 3-х кратного избытка K_2CO_3 в среде ацетона при температуре 60 ºС. Реакцию пропаргилирования ксантагенатов натрия проводили бромистым пропаргилом в среде ацетона при комнатной температуре. *Заключение.* В результате реакций синтезированы карбонодитиоаты, тиоангидриды, ацетиленовые и тиоацетиленовые эфиры на основе О-ароматических систем (4-гидроксибензальдегида и 4-гидрокси-3-метоксибензальдегида). Строение синтезированных соединений установлено на основании данных элементного анализа, ИК спектров, спектроскопии ЯМР ^{1}H и ^{13}C.

Ключевые слова: ксантогенаты натрия, тиоангидриды, пропаргилирование, ацетиленовые и тиоацетиленовые эфиры

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