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SYNTHESIS AND ROOT-FORMING ACTIVITY OF DITHIOCARBAMATES BASED ON THE 2-(METHYLAMINO)ETHANOL AND QUINOLINE-8-OL

Abstract. New biologically active potassium and sodium dithiocarbamates were synthesized by the interaction of 2-(methylamino)ethanol and quinoline-8-ol with carbon disulfide in the presence of solutions alkali in ethanol at room temperature. As a result of the reaction sodium 2-hydroxyethyl(methyl)carbamodithioate (70%) and potassium O-quinolin-8-yl-carbonodithioate 2 (86%) were obtained. The structure of the synthesized compounds was established based by the data of elemental analysis, IR and NMR (^{1}H and ^{13}C) spectroscopic data. Field tests showed that the treatment of seedlings with dithiocarbamates activates the formation of the root system and shoots in comparison with the control group. The most effective was potassium O-quinolin-8-yl-carbonoditioat, which at a concentration 0.01% obtaind profound results in terms of root length about – 8 cm, the average number of formed shoots – 1,6, and an average length of the shoots at 1,4 cm.

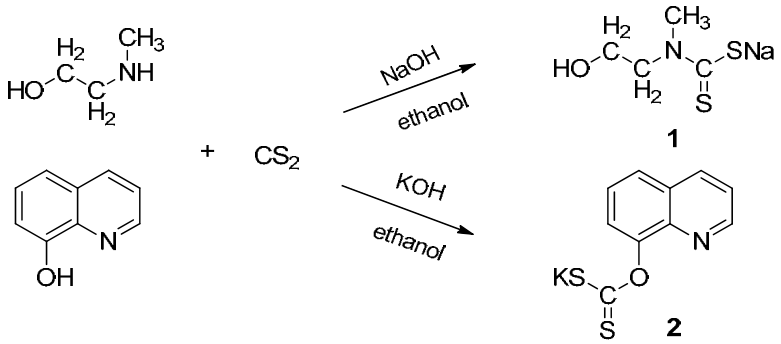
Keywords: 2-(methylamino)ethanol, quinoline-8-ol, carbon disulfide, dithiocarbamates, NMR (^{1}H and ^{13}C) spectroscopy, root-forming activity.

Dithiocarbamates and their derivatives are known as compounds,possessing antimicrobial, anti-inflammatory, flotation, herbicidal and fungicidal activity [1-4]. At the A.B. Bekturov Institute of Chemical Sciences over the past ten years, have been conducted studies on the synthesis of new derivatives of dithiocarbamates and on the search among them of new biologically active compounds. Previously, among the synthesized dithiocarbamate derivatives that we synthesized, substances with flotation and growth-stimulating activity were identified [5, 6].

In continuation of our research, we synthesized dithiocarbamates based on 2-(methylamino)ethanol and quinoline-8-ol, which have root-forming activity [7,8]. Potassium and sodium dithiocarbamates were synthesized by reacting 2-(methylamino)ethanol and quinoline-8-ol with carbon disulfide in the presence of alkali in ethyl alcohol at room temperature.

The course of the reactions were controlled by the method of thin-layer chromatography (TLC) on silicagel. As a result of the isolation from the reaction mixtures, sodium 2-hydroxyethyl(methyl)carbamodithioate**1** (70%) and potassium O-quinolin-8-yl-carbonodithioate **2** (86%) were obtained in an individual form with the corresponding yields.

The structures of the synthesized compounds **1**, **2** were established based on the data of elemental analysis, IR spectroscopy and ^{1}H and ^{13}C NMR spectroscopy (tables 1, 2).



In the IR spectra of compounds**1**, **2** the absorption band of stretching vibrations of the C = S group appear in the region 1093, 1047 cm^{-1}. Valence vibrations of the C – S bond present in the region 659, 676 cm^{-1} (table 1).

Table 1 – Physicochemical characteristics of dithiocarbamates **1**, **2**

Comp.	Yield, %	R_f, Eluent	Found, % Calculated, %				IR Spectrum, ν, cm^{-1}		Formula
			C	H	N	S	C=S	C-S	
1	70	0,81 (dioxane)	27,99 27,73	4,83 4,65	8,25 8,09	36,87 37,02	1093	659	$C_4H_8NNaOS_2$
2	86	0,31 (water)	46,71 46,30	2,61 2,33	85,03 85,40	24,29 24,72	1047	676	$C_{10}H_6KNOS_2$

Table 2 – ^1H and ^{13}C NMR spectral data for dithiocarbamates **1**, **2**

Comp.	NMR ^1H (δ, ppm)		NMR ^{13}C (δ, ppm)	
	OH	CH, CH_2, (CH_3)	C=S	CH; CH_2; CH_3
1	4,67	2,88; 3,68; (2,51)	174,98	57,12; 58,00; 41,92
2	–	7,25; 7,70; 8,10; 8,42	160,94	147,36 ($C^{2,8}$); 143,53 (C^9); 135,90 (C^4); 133,86 ($C^{3,6}$); 127,88 (C^{10}); 121,91 ($C^{5,7}$)

In the PMR spectra of compound **1 there** are found signals of the methyl group protons in the region δ 2,51 ppm, the protons of the methylene groups at δ 2,88 and 3,68 ppm. The proton of the hydroxyl group resonates as a singlet in the regionδ 4,67 ppm. In the ^{13}C NMR specta present the carbon atom signal of the C = S bond in the weak field δ 174,98 ppm. The carbon atoms of the methylene CH_2 groups resonate at δ 57,12 and 58,00 ppm. The methyl carbon atom resonate in the region δ41,92 ppm.

In the PMR spectra of compound **2** the protons of the quinoline ring resonate in the weak field region δ 7,25; 7,70, 8,10; and 8,42 ppm. In the ^{13}C NMR spectra

the carbon atom signal of the C = S bond appear in the weak field region δ 160,94 ppm. The carbon atoms of the quinoline ring resonate in the region δ 147,36 ($C^{2,8}$); 143,53 (C^{9}); 135,90 (C^{4}); 133,86 ($C^{3,6}$); 127,88 (C^{10}) and 121,91 ($C^{5,7}$).

The study of the root-forming activity of the synthesized compounds **1**,**2** was carried out on the sprout of spirea (Spiraeasalicifolia) [7, 8]. Experiments on the study of the influence of growth regulators on the growth and development of the root system of the sprout of the willow spirea were conducted in the Institute of Botany and Phytointroduction.

Before planting, the sprouts were kept in the solutions with concentrations of 0,01%, 0,001% with an exposure of 6 hours when the ends of the sprouts were immersed in the solution. Then the sprouts were planted in a prepared greenhouse in the soil, covered from above with medium-grained river sand. The sand layer was 1.5 cm. The duration of the experiment was 3 months.

The experiment was carried out according to the scheme: 1. Control (without treatment). 2. Analog (KH-2) with concentrations of 0,01%, 0,001%. 3. Compounds **1**, **2** with concentrations of 0,01%, 0,001%. The results of the experiment are presented in the table 3.

Table 3 – Influence of dithiocarbamates **1**, **2** on the rooting of the spirea sprouts

Compounds and their concentrations, %	Number of root forming centers	Length of roots, cm	Number of shoots	Length of shoots, cm
Control (water)	2,1	4,1	0,9	1,2
KH-2 (0,01%)	1,7	5,3	0,7	0,8
KH-2 (0,001%)	2,2	6,3	1,0	0,9
1 (0,01%)	2,4	5,3	1,1	1,6
1 (0,001%)	2,2	6,4	1,3	1,6
2 (0,01%)	2,1	8,0	1,6	1,4
2 (0,001%)	2,4	6,5	1,1	1,0

It should be noted,that comparing the four parameters, in the three parameters dithiocarbamates**1**, **2** showed a high result in comparison with the control and the reference standard KH-2 (table 3).

Thus, the number of root centers, the length of the roots, the number and length of the formed shoots in the control were 2,1 cm, 4,1 cm, 0,9 pieces and 1,2 cm, respectively, for the preparation KH-2 at a concentration 0,01% - 1,7 cm, 5,3 cm, 0,7 pieces and 0,8 cm, but using compound **1** - 2,4 cm, 5,3 cm, 1,1 pcs and 1,6 cm and compound **2** – 2,1 cm, 8,0 cm, 1,6 pcs and 1,4 cm.

At a concentration of 0,001% the number of root-forming centers, the length of the roots, the number and length of the formed shoots for the preparation KH-2 were, respectively, 2,2 cm, 6,3 cm, 1,0 pieces and 0,9 cm, for compound **1** – 2,2 cm, 6,4 cm, 1,3 pieces and 1,6 cm, and using compounds **2** – 2,4 cm, 6,5 cm, 1,1 pieces and 1,0 cm.

It was established that the treatment of seedlings with dithiocarbamates **1**, **2** activates the formation of the root system and shoots in comparison with the control and the reference standard KH-2. When treating the sprouts, potassium O-quinolin-8-yl-carbonodithioate **2** turned out to be the most effective, which, at a concentration of 0.01%, showed a good result along the root length - 8 cm, the number of formed shoots was 1.6 and the average length of these shoots was 1.4 cm.

Thus, as a result of the conducted research, new sodium 2-hydroxyethyl (methyl)carbamodithioate and potassium O-quinolin-8-yl-carbonodithioate, possessing root-forming activity were synthesized. It was established that the studied growth regulators have high biological activity and can be used in the technology of accelerated cultivation of planting material.

EXPERIMENTAL

The course of the reaction and purity of the products were monitoredby TLC analysis on “Silufol UV-254” plates, eluent was ethanol - benzene (1:3). Elemental analysis was performed on the CE 440 elemental analyzer. The IR spectra of synthesized compounds were recorded on a Nicolet 5700 spectrometer in KBr tablets. The ^{1}H and^{13}C NMR spectra were recordedon a JNM-ECA 400 (Jeol) spectrometer in D_2Osolution.

Sodium 2-hydroxyethyl(methyl)carbamodithioate (1). A solution of 2,02 g (0,026 mol) carbon disulfide in 10 ml of alcohol was added dropwise with stirring to a solution of 2 g (0,026 mol) 2-(methylamino)ethanol and 1,06 g sodium hydroxide in 15 ml of alcohol cooled to -5 °C. The reaction mixture after the addition of carbon disulfide was stirred for 2 hours. The solvent was distilled off under reduced pressure and the solid residue was purified by recrystallization from benzene. Sodium 2-hydroxyethyl(methyl)carbamodithioate **1**was obtained in 3,2 g (70%) yield.

Potassium O-quinolin-8-yl-carbonodithioate (2).A solution of 3,8 g sodium hydroxide in 10 ml of distilled water was added to a solution of 10 g (0,068 mol) quinoline-8-ol in 30 ml of alcohol. Then a solution of 5,2 g (0,068 mol) carbon disulfide was added dropwise at a temperature 0-5 °C. Then the temperature of the reaction mixture was slowly raised to room temperature. The reaction mixture was stirred at room temperature for four hours. The solvent was distilled off under reduced pressure and the solid residue was purified by recrystallization from benzene. Potassium O-quinolin-8-yl-carbonothioate **2** was obtained in14,86 g (86%) yield.

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Резюме

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2-(МЕТИЛАМИНО)ЭТАНОЛДЫҢ ЖӘНЕ
ХИНОЛИН-8-ОЛДЫҢ ДИТИОКАРБАМАТТАР СИНТЕЗІ
ЖӘНЕ ОЛАРДЫҢ ТАМЫРЛАНДЫРҒЫШ АКТИВТІЛІГІ

Жаңа биологиялық активті калий және натрий дитиокарбаматтары 2-метиламиноэтанолдың және хинолин-8-олдың күкірткөміртекпен сілті қатысында бөлме температурасында әрекеттесуі арқылы синтезделініп алынды. Реакция нәтижесінде натрий 2-гидроксиэтил(метил) карбамодитиоаты (70%) және калий О-хинолин-8-илкарбонодитиоаты 2 (86%) бөлініп алынды. Синтезделген 1,2 қосылыстардың құрылысы элементтік талдау, ИҚ-спектроскопия және ЯМР 1Н және 13С спектроскопиясы негіздерінде дәлелденді. Тамырландырғыш активтілікке жүргізілген сынақ иволистті спирея көшеттерін 1, 2 дитиокарбаматтарымен өңдеу тамыр жүйесін және өскіндерді активтендіргенінкөрсетті. Калий О-хинолин-8-ил-карбонодитиоатының 2 эффективтілігі жоғарыекендігі 0,01% концентрацияда тамыр ұзындығы бойынша ең жоғары нәтиже – 8 см көрсетті, түзілген өскіндердің саны – 1,6 және осы өскіндердің орташа ұзындығы -1,4 см.

Түйін сөздер: 2-(метиламино)этанол, хинолин-8-ол, күкірткөміртек, дитиокарбаматтар, ^{1}Н және ^{13}С ЯМР спектроскопия, тамырландырғыш активтілік.

Резюме

Е. С. Сычева, М. С. Муканова, Ж. А. Рахимбеков, В. К. Ю, Г. С. Муканова

СИНТЕЗ И КОРНЕОБРАЗУЮЩАЯ АКТИВНОСТЬ ДИТИОКАРБАМАТОВ НА ОСНОВЕ 2-(МЕТИЛАМИНО)ЭТАНОЛА И ХИНОЛИН-8-ОЛА

Новые биологически активные дитиокарбаматы калия и натрия синтезированы взаимодействием 2-(метиламино)этанола и хинолин-8-ола с сероуглеродом в присутствии раствора щелочи в этаноле при комнатной температуре. В результате реакций были выделены 2-гидроксиэтил(метил) карбамодитиоат натрия (70%) и О-хинолин-8-илкарбонодитиоат калия 2 (86%). Структура синтезированных соединений 1, 2 установлена на основании данных элементного анализа, ИК-спектроскопии и спектроскопии ЯМР ^{1}Н и ^{13}С. Испытания на корнеобразующую активность показали, что обработка черенков спиреи иволистной дитиокарбаматами 1, 2 активизирует формирование корневой системы и побегов. Наиболее эффективным оказался О-хинолин-8-ил-карбонодитиоат калия 2, который при концентрации 0,01% показал высокий результат по длине корней – 8 см, количество образовавшихся побегов 1,6 и средняя длина этих побегов составила 1,4 см.

Ключевые слова: 2-(метиламино)этанол, хинолин-8-ол, сероуглерод, дитиокарбаматы, спектроскопия ^{1}Н и ^{13}СЯМР, корнеобразующая активность.