Synthesis of 3-Hydroxypyridine and their Bio Growth Promoting Activity

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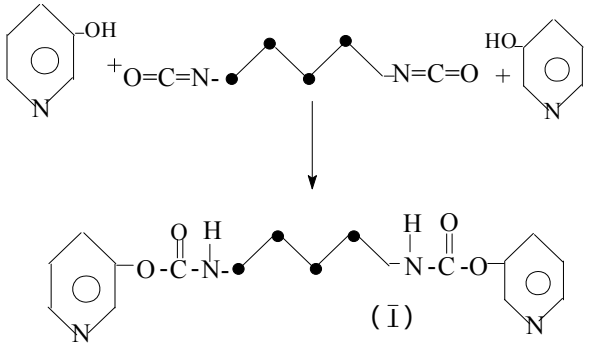
Abstract

The article presents the synthesis of N, N[1]-tetramethylene bis [(3-hydroxypyrido) carbamate] and its derivatives. Physico-chemical constants were defined, synthesized compounds structure by elemental analysis and IR spectroscopy were identified, and the results of bio growth stimulating active preparations for vegetable crops and cotton were found out. It is found out that among the studied chemical drugs the most highly effective bio growth stimulating for cotton and vegetable crops were N, N[1]-butylene-bis-[(3-hydroxypyridyl) carbamate] at a concentration of 0.001% solution.

Keywords: N, N[1]-tetramethylene bis[(3-hydroxypyrido) carbamate], IR spectroscopy, N, N[1]-butylene-bis - [(3-hydroxypyridyl) carbamate]

Introduction

At the present time, the analysis in the scientific literature, monographs and patent literature shows that the synthesis and development of technology selective, high-performance, low-cost, low-toxic, ecologically clean perspective 3-pyridyl bis-carbamates is the subject of active research laboratories and companies in several foreign countries [1-7], including Uzbekistan [8-11]. The purpose of this message is to decrease toxicity, labor intensity, cost-effective and ecologically clean bio reception preparation of growth-regulating, low cost production method, availability, even without the cost of electricity and high yields, providing super growth-regulating properties of technical and vegetable crops (cucumbers, tomatoes, sunflower, corn, soybeans) and cotton. In addition, the brief is based on the development of cognitive skills of young researchers investigated in this promising area. The object is achieved the goal of waste-free technologies ecologically clean developing of obtaining previously is non described bio growth-regulating N, N[1]-tetramethylene bis[(3-hydroxypyridyl) carbamate], by the following reaction scheme:



Experimental

Synthesis of N, N-one disodium substituted tetramethylene bis [(3-hydroxypyridine) carbonate]

The flask was fitted with a reflux condenser with a calcium chloride tube, auto stirrer, thermometer placed CH_3ONa (of 0,031g / mol of Na and 30 ml of absolute methanol) is added 3.3g (0.01mol) tetra methylene bis [(3-hydroxypyridyl) carbamate]. Mixing mixture for 2 hours at 22^0C and 2 hours at 40-42 ^{0}C, the precipitate was filtered, washed with absolute methanol to afford N, N | -dinatrium tetra methylene bis [(3-hydroxypyridyl) carbamate]. Exit-2.93 g (78.3%). Trazl-347 ^{0}C. Found, %: N 14,66; Calculated for $S_{16}H_{16}Na_2N_4O_4$, %: N 14,97.

Synthesis of N, N-non benzoylation 1 tetramethylene bis [(3-hydroxypyridine) carbamate]

In a flask equipped with a reflux condenser, a thermometer, a stirrer and cars are placed 3,47g (0,01 mol) N, N^1-disodium tetra methylene bis [(3-hydroxypyridyl) carbamate] in 14 ml of DMF. With slow stirring, was added drop wise 4.36 ml (0,02 mol) benzyl iodide. The mixture was then stirred for 9-10 hours on a boiling water bath. Cool and pour 25-30 ml of water, the precipitate is recrystallized from 50% alcohol and dried to give -4,66 g (91.4%) mp = 166-167^{0}C (sm.tabl.3).

Synthesis of N, N-nonnitration 1 tetra methylene bis[(3-hydroxypyridine) - carbamate]

In a flask equipped with a reflux condenser, a thermometer, a stirrer was placed, 3,3g (0,01mol), dissolved in 200 ml of formic acid, tetra methylene bis [(3-hydroxypyridyl) - carbamate]. With constant stirring, at a temperature 0-4^{0}C added portion wise 0.6 g of sodium nitrite in excess for 4.0 hours. After finishing reaction product was poured into a liter beaker was added 500 ml of cold water; filtered N, N-non nitro compounds, installed on TLC plates «Silifol».

Exit-3.58 g (93.2%). M.p 2100S (dec.) (Sm.tabl.3).

Synthesis of N, N-1 nonchlorination tetra methylene bis [(3-hydroxypyridine) - carbamate]

The flask was fitted with a reflux condenser with a calcium chloride tube, a thermometer is placed, 3,3g (0,01 mol), tetra methylene bis [(3-hydroxypyridyl) - carbamate], 50 ml of chloroform, 20 g of wet alumina and added dropwise 4,4g calcium hypochlorite at a temperature 40 ^{0}C for 1.5 hours. The reaction mixture is allowed to stand for 22 hours. Filtered, the residue washed with ether, alcohol such as give N, N^1-dichloro tetramethylene bis[(3-hydroxypyridyl) - carbamate] Exit-3.58 g (96.1%). M.p 74-75 ^{0}C (see Table .3)

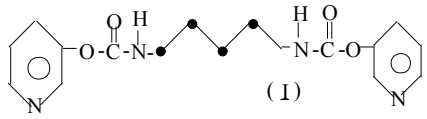
To prove the structure of N, N^1-dichloro tetra methylene bis [(3-hydroxypyridine) - carbamate] conducted elemental analysis with silver salt ($AgNO_3$ solution). Thus, the technology of obtaining N, N^1-tetra-bis - [(3-hydroxypyrido) carbamate] and studied its chemical properties of N-H reaction centers: metalation reaction, alkylation nitration, chlorination.

Results and Discussions

Personality of obtained previously non described product was checked by TLC on a fixed layer (Al_2O_3), a second degree of purity in the system. Drug I was prepared by the following steps: mixing, washing, drying, cleaning, which takes about 2.5 hours time. To prove the structure of the compound I, besides elemental analysis to remove IR Spectrum. In the IR-spectrum contains absorption bands are characteristic fluctuations: -NHCOO - 1644 cm^{-1}; $-CH_2$ - 2927 cm^{-1}; $-(CH_2)_4$- 754-718 cm^{-1}.

Physico-chemical characteristics of the derivative of bis [(3-hydroxypyridine) carbamate] shown in Table 1.

Table 1. Physical and chemical characteristics of drug I

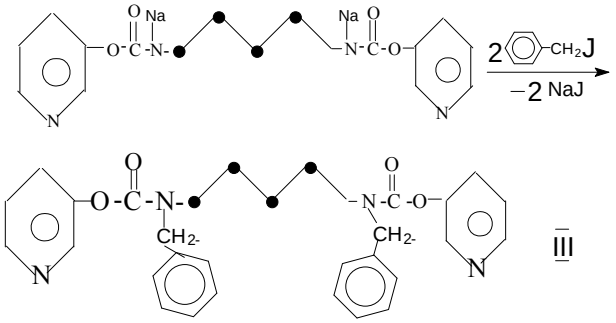
Structural formula	Exit , %	T. Пл., ^{0}C	R,f	Brutto formula	Elemental analysis, %					
					Calculated			Found		
					C	H	N	C	H	N
N,N^1- tetra methylene bis [(3-hydroxypyridine) carbamate]  (I)	97,3	169-170	0,74	$C_{16}H_{18}N_4O_4$	58,18	5,45	16,97	58,34	5,39	16,81

Further, it was investigated the chemical converting the derivative of N, N^1-tetra methylene bis [(3-hydroxypyridyl) carbamate];

N, N^1- non methylation; -nonalkylation; nonchlorination and nonnitration.

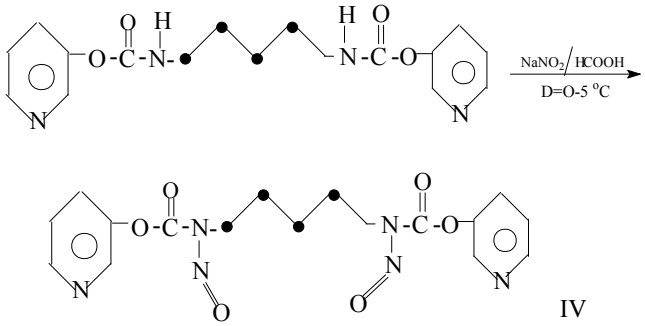
N, N^1-nonmetalation: reacting SN_3ONa in absolute CH_3OH with a preparation obtained I N, N^1-disodium derivatives I, (II).

N, N^1-nonalkylation: Synthesis of N, N^1-I disodium benzyl iodide formed with N, N1-dibenzil-, N, N^1-tetramethylene bis [(3-hydroxypyridyl) carbamate] (III) according to the following scheme below:



III

N^1 N^1-nonnitrosation: Analogously, by reaction with sodium nitrite in formic acid at a temperature of 0-5 ^{0}C for 3.5 h are obtained IV preparations:

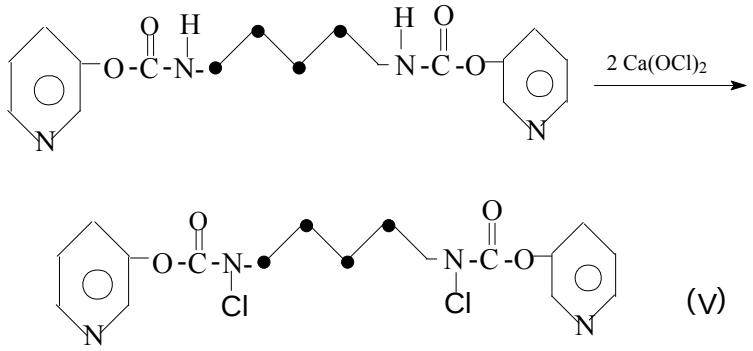


IV

g) N^1-N^1 nonchlorination:

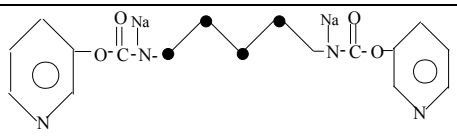
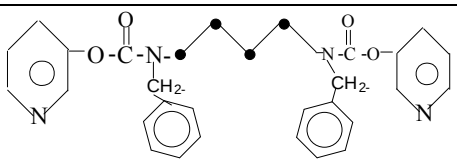
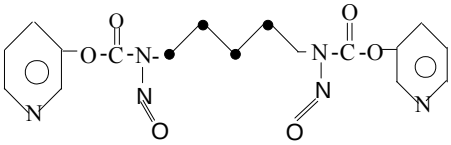
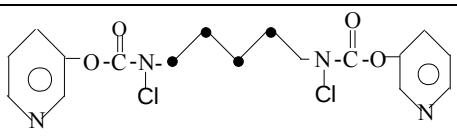
N^{1}N^1-nonchloro- N^1 N^1-buthylene bis [(3-hydroxypyridine) carbamate] V were obtained:

Interaction of preparation I with hypochlorite calcium on reaction scheme:



Physico-chemical characteristics of the obtaining chemical reactions are shown in Table 2.

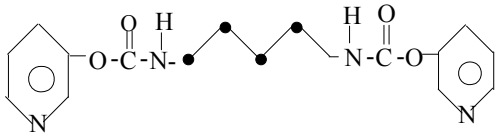
Table 2 Physical and chemical characteristics of derivatives II-V drugs

№	Structural Formula	Exit, %	tm, ^{0}C	Brutto formula	Elemental analysis, %						M_M
					Calculated			Found			
					C	H	N	C	H	N	
II	 N, N1-disodium-N, N1-tetramethylene bis [(nicotinoyl) carbamate]	87.8	230 (разл)	$C_{16}H_{16}Na_2N_4O_4$	51,33	4,27	14,97	51,17	4,03	14,74	374
III	 N,N^1-Dibenzyl -N,N^1-tetramethylene bis [(nicotinoyl) carbamate]	91.4	166-167	$C_{30}H_{30}N_4O_4$	70,58	5,88	10,98	70,33	5,23	10,73	510
IV	 N,N1-dinitroso-N,N1-tetramethylene bis[(nicotinoyl) carbamate]	93.2	210 (разл)	$C_{16}H_{16}N_6O_6$	49.48	4,12	21,65	49,33	4,06	21,56	388
V	 N,N^1-dichloro-N,N^1-tetramethylene bis [(nicotinoyl) carbamate]	96.1	74-75	$C_{16}H_{16}Cl_2N_4O_4$	48.12	4,01	14,04	47,88	3,84	13,85	399

To identify biological growth-stimulating activity of bis [(3-hydroxypyridine) carbamate]. The drug was tested in the laboratory phitotoxicology IHRV RUz Biotest served vegetable seeds and cotton primary cracking was conducted by the method Yu.V.Rakitina.

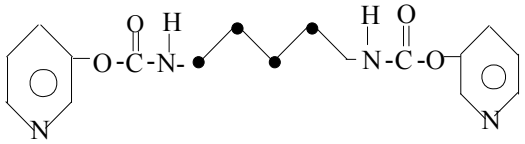
This method allows fairly quickly determine the degree of physiological activity of chemical compounds, which is detected by stimulation or inhibition of the germination of plant seeds, as well as to change the length of the roots and the length of the stems. Drugs are tested by steeping the seeds in solutions of various concentrations, followed by germination in Petri dishes, test the seeds were soaked in distilled water. It is found that when cotton clasp N, N^1-tetra methylene bis [(3-hydroxypyridyl) carbamate] at 0.1; 0.01; 0.001% the drug contributed to the increase in seed germination, ahead of control of the studied drugs on the growth promoting activity of bio cotton. It showed that the drug contributed to the development of the root system of the seedling at a concentration of 0.001%, accelerates the ability to seed on the fifth day to several times higher than the control (Table. 3)

Table 3. Biotest of cotton plant

Structural formula	concentration, %	Seed germination after 5 days,%	Growth preparations on 10 th day,%	
			Root	Stem
	0,1	80	122,3	109,6
	0,01	80	143,4	118,4
N^1N^1-tetrametilen bis [(3-hydroxypyridine) carbamate]	0,001	80	131,2	113,3
Control- H_2O		80	100	100
"Roslyn" - the famous	0,75	80	103,5	94,3

The preparation of bis [(3-hydroxypyridine) carbamate] at a concentration of 0.001% (ie, 7,500 times dilution) stimulated germination seedling cotton plant 143% above control and root growth 131.2% and 113.3% growth of the stem higher than the control (Table. 3)

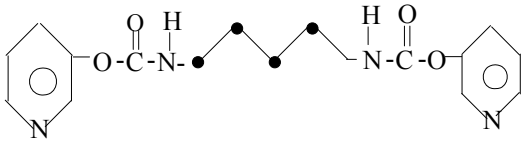
Table 3 Biotest of tomato

Structural formula Name	concentration, %	Seed germination after 5 days,%	Growth preparations on 10 th day,%	
			Root	Stem
	0,1	41	122,3	111,6
	0,01	52	129.7	116.8
N1 N^1-buthylene bis [(3-hydroxypyridine) carbamate]	0,001	54	148.7	123,1
KControl- H_2O	б/о	30	100	100
"Roslyn" - known drug	0,75	40	100	100

The preparation of bio grow stimulant N^1N^1-buthylene-bis - [(3-hydroxypyridine) carbamate] at a concentration of 0.001% (ie, 7,500 times dilution) stimulated germination of tomato seedlings 180% above control and root growth 148.7% and stem growth to 123.1% higher than the control (Table. 3)

Experiments on cucumber varieties "Uzbekistan-740" showed that the formulation of the active influence on the growth of the root system of seedlings (Table 4)

Table 4. Biotest of cucumbers

Structural formula	Concentration, %	Seed germination after 5 days, %	Growth preparations on 10 th day,%	
			Root	Stem
	0,1	100	117.6	112.4
	0,01	100	128.7	119.6
N1N1- buthylene bis [(3-hydroxypyridine) carbamate]	0,001	100	142.6	124.5
Control- H_2O	б/о	100	100	100
"Roslyn" - known drug	0,75	100	101.3	98.7

Thus, the preparation N, N^1-buthylene-bis-[(3-hydroxypyridine) of carbamide] at a concentration of 0.001% were the most highly bio grows simulate for vegetable crops and cotton in-depth study in laboratory conditions, Andijan and Kashkadarya regions.

Conclusion

The paper presents the results of the synthesis of N, N1-tetra methylene bis [(3-hydroxypyridyl) carbamate] and derivatives thereof determined by the physicochemical constants set structure of the synthesized compounds by elemental analysis and IR spectroscopy and the results biorostostimuruyuschey active preparations for vegetable crops and cotton. It is found that among the studied drugs the most highly bio growth-stimulating activity. Vegetable and cotton crops were N, N^1-butylene-bis -[(3-hydroxypyridyl) carbamate] at a concentration of 0.001% solution.

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