International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2019; 7(3): 870-872

Received: 22-03-2019
Accepted: 26-04-2019

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Growth stimulant of silkworm

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Abstract
One of the economically valuable insects is silkworm the rapid change of growth phases of which makes it an interesting object of researches on growth subject and development of larvae. Apart from antitumor activity synthesized organoselenium compound 2-dibutylaminoselenol-1("selenol") exhibited growth stimulant properties of a silkworm. Among organoselenium compounds sodium salt of selenious acid (Na_2SeO_3) is the most common as the growth stimulant of silkworm. Advantage of sodium selenite over other stimulants is its effectiveness at small concentration on live weight of caterpillars (totally 30-40 mg for 1 kg of live weight). Disadvantage of using selenite is shown in lower value of silk-screening, activity of caterpillars, productivity of cocoons from a box of caterpillars. Therefore, while conducting researches to study the stimulation properties of "selenol" we compared actions of the latter to the data of sodium selenite. To carry out experiments "selenol" was dissolved in distilled water (6 mg of medicine for 1 kg of live weight of caterpillars) and mulberry leaves were sprayed with the solution. It is should be emphasized that "selenol" consumption is 5-6 times less by weight than the consumption of sodium selenite. Caterpillars were fed on these leaves from 2^d day of 4th age, at each age - 1 time (only 2 times). Feeding of caterpillars was carried out in threefold replication of each group for 150 caterpillars. Tests of "selenol" as a biostimulator of a silkworm were performed at 12 sites (kumkhana – small industrial farms). As a result of using this medicine it was possible to get a good harvest: 267 kg harvest was got per 95 g of a grain (a grain – eggs of silkworm moth). Given that annual average plan of a small farm makes 15 tonnes, then the increase in a harvest of cocoons using "selenol" will make about 790 kg.

Keywords: Silkworm, caterpillar, growth stimulant, "selenol"

Introduction
Intensive researches on chemistry of organoselenium compounds were preceded by revealing the mechanism of their influence and a variety of important and useful properties of these compounds. The high bioactivity and antioxidant properties contributed the creation of medicines for the treatment of cardiovascular, allergic and cancer diseases on the basis of organoselenium compounds. Authors of this article found the study of physiological activity (studying the stimulation properties) of organoselenium compounds with selenohydrile group – 2-dibutylaminoselenol-1 ("selenol") on the sample of silkworm cocoons to be interesting. Silkworm is one of the economically valuable insects. Rapid change of growth phases: graine (egg) – larva - pupae - butterfly make it very interesting object of researches (Harborn J. 1985) [1]. There are a number of works on the creation of highly productive breeds of a silkworm and stimulation of their growth (Shkaruba N.G. 1993; Leinveber E.F. 2010; Bakirov M.Y. 1981) [3, 4, 5]. In some works it is recommended to perform spraying of silkworm caterpillars with 3% solution of formaldehyde (Salijanov S. 2011) [6] or the medicine consisting of sulfur and synthetic detergents (Azimov D.A. *et al*. 1995) [7]. A number of works present the data on forecasting the efficiency of a silkworm on enzyme systems and protein spectra (Bogoslovskiy V.V. 2009) [8]. Ethyl ether (2, 4 E) - 3-methyldeca -2,4-diene acid is used as regulators of growth and development of larvae of a silkworm (Kukovints O.S. *et al*. 1993) [9]. Among selenium compounds sodium salt of selenious acid (Na_2SeO_3) is the most common as the growth stimulant of silkworm. Advantage of sodium selenite over other stimulants is its effectiveness at small concentration on live weight of caterpillars (totally 30-40 mg for 1 kg of live weight). Disadvantage of using selenite is shown in lower value of silk-screening, activity of caterpillars, productivity of cocoons from a box of caterpillars. Therefore, while conducting researches to study the stimulation properties of "selenol" we compared actions of the latter to the data of sodium selenite. Researches revealed that "selenol-1" exhibited the properties of antitumor agent which suppresses tumor growth. In case of using this medicine the fields of its application will be expanded.

"Selenol" was obtained using developed technique with the reaction of dichloroethane (DCE), sodium selenide (Na_2Se) and secondary amine (dibutylamine, DBA) with a good yield (60-70%):

$$\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix} + Na_2Se + (C_4H_9)_2NH \quad HSeCH_2CH_2N(C_4H_9)_2 + 2NaCl$$

Reaction was carried out at a molar ratio of reacting components (DCE: DBA: Na_2 Se = 0.3:0.25:0.2), at boiling temperature 95-105^0 C, duration of 4 hours in inert gas atmosphere (nitrogen). Originally, the reaction was conducted without using a catalyst.

Methods and Materials

Synthesis of 2-dibutylaminoselenol-1 25 g (0.2 g/mol) of Na_2Se and 30 g (0.25 g/mol) of DBA, 2g (18-C-6-E) and 50 ml of DMF are put into a flask in a stream of nitrogen. The mixture is heated till 80^o C and 30 g (0, 32 g/mol) of dichloroethane is added drop by drop for 0.5 hours from funnel at this temperature. Then the temperature is increased to 90^{o}C and mixing is continued for 3,5 hours. At the end the reaction mixture is cooled and filtered in Buchner funnel. Crystalline mass is dissolved in ethanol; filtered and sulphuric ether is added into filtrate to crystallize the target product during cooling till 0^{o}C. 39 g of «selenol» (80% from the theory for Na_2Se) is obtained with T_{boil}. 283-285^{o}C. IR spectrum (cm^{-2}): 2290(-Se-H), 560, 1200 (CH_2), 740-760(C-Se-). Letter symbols were used for correlation of proton signals in NMR spectrum of (δ, ppm) "selenol":

d c b a
g f e
$H\text{-}Se\text{-}CH_2\text{-}CH_2\text{-}N$ $<$ $CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$, $CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

a = 0,85 c (3H, - CH_3)
2 (b,c), f = 1,3-1,75 m, (4H, - CH_2-)
2d, c = 2,82 – 3,2 d (4H, - N-CH_2)
g = 4.8 c (1H, H – Se-)

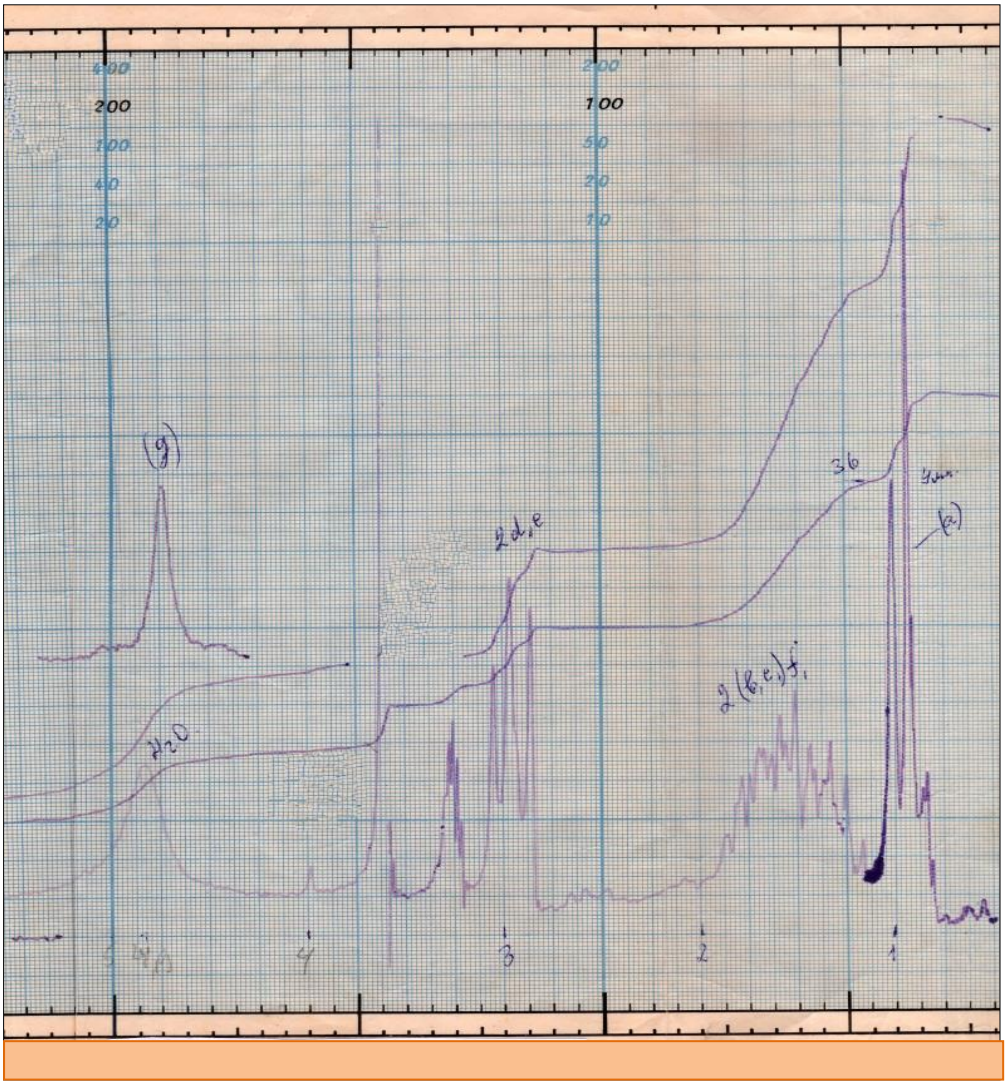

Fig 1: NMR spectrum of 2-dibutylaminoselenol-1

Results and Discussion

It was found that the process proceeds relatively smoothly in the environment of aprotic solvent – dimethyl formamide (DMF) capable of solvating sodium selenide solvation. Advantage of the offered method over the known ways of obtaining aminoethanselenol is that unlike multistage method it allows obtaining target medicine "selenol" in one stage using available initial compounds. To improve the conditions of carrying out the reaction we used the method of interphase catalysis which, as we know, allows easy course of various reactions on the border "solid phase - liquid". In particular, such catalysts like triethylammonium chloride (TEBAH) and

18-crown-6-ether (18-C-6-E) were used for above mentioned reaction. Among these catalysts the use of 18-crown-6-ether was more preferable, since it increased the yield of target product (80-85% against 60-70%) at lower temperature (temperature of reaction was reduced to 80-90^{o}C against 95-105^{o}C).

To carry out experiments "selenol" was dissolved in distilled water (6 mg of medicine for 1 kg of live weight of caterpillars) and mulberry leaves were sprayed with the solution. It is should be emphasized that "selenol" consumption is 5-6 times less by weight than the consumption of sodium selenite. Caterpillars were fed on these leaves from 2^{d} day of 4th age, at each age - 1 time (only 2 times). Feeding of caterpillars was carried out in threefold replication of each group for 150 caterpillars. Tests of "selenol" as a biostimulator of a silkworm were performed at 12 sites (kumkhana – small industrial farms). As a result of using this medicine it was possible to get a good harvest: 267 kg harvest was got per 95 g of a grain (a grain – eggs of silkworm moth). Given that annual average plan of a small farm makes 15 tonnes, then the increase in a harvest of cocoons using "selenol" will make about 790 kg. Comparative analysis of table data revealed that stimulating properties of "selenol" surpass those in sodium selenite: bave reelable length increases by 68 m, harvest of cocoons increases by 8%, yield of a raw silk increases by 5%, longevity increases more than twice. Table data confirmed once again that some organoselenium compound with antitumor activity exhibit physiological activity.

Table 1: Properties of growth stimulators of silkworm of sodium selenite and selenol

Medicines	Silkiness %	Yield of raw silk, %	Bave Reelable length, m	Mass of alive cocoon	Viability%	Productivity of cocoons from caterpillars, kg	Intensity of breaking MPa	Longevity c
Na_2SeO_3	42,6	37,5	622	2,15	97,6	92	600	85
«selenol»	45.5	39,7	690	2,23	99,8	100	660	180

BRL – bave reelable length

Longevity - time from the moment of loading the sample till its breaking (τ = 550 MPa)

One box of a grain contains 29 eggs. Averagely 56-57 kg cocoons are obtained from one box of a grain.

In particular, the use of "selenol" as a biostimulator of a silkworm allows increasing the efficiency of caterpillars, improving quality of a thread that will result in the considerable economic effect.

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