

ASSESSMENT OF THE BIOLOGICAL EFFECT OF 2,2-PROPAGYLOXY BENZOIC ACID ON GRAINS OF SINGLE AND DICOTYLEDONOUS PLANTS

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Abstract: *Introduction.* Oxygen heterocyclic compounds occupy an important place in modern organic and medical chemistry. Tetrahydropyran derivatives in particular are widely studied due to their structural diversity and biological activity. In this regard, the problem of agronomy and phytochemistry is to determine the biological activity of propargyloxybenzoic acid, an oxygenated derivative of 2,2-dimethyltetrahydropyran-4 — on and propargylated salicylic acid in the grains of single and dicotyledonous plants by the reaction of Favorsky. *The purpose and objectives of the work* is to study the biological activity of seeds of single and dicotyledonous plants with the synthesis of a new oxygenated heterocyclic compound based on 2,2-dimethyltetrahydropyran-4-on and propargylated salicylic acid. *Tasks* obtaining the original compound by The Prince reaction, synthesizing a new derivative using the Favorsky reaction, and studying its biological activity. *Conclusion* (conclusions). The oxygen heterocycle 2,2-dimethyltetrahydropyran-4-on was obtained with dimethylvinyl-ethylcarbinol in a sulfuric acid medium and using mercury sulfate as a catalyst, with a yield of 70% through the Prince reaction mechanism. By reacting the resulting 2,2-dimethyltetrahydropyran-4-on with the acetylene derivative of salicylic acid by the Favorsky reaction, the acetylene derivative of 2,2-dimethyltetrahydropyran-4-on was synthesized with a 57% yield of 2,2-propagyloxy benzoic acid. The physicochemical properties of the obtained oxygen heterocycle compounds were determined and studied by IR spectroscopy. According to the results of a study of the biological activity of 2,2-propagyloxy benzoic acid on single and dicotyledonous plant grains, it was found that it significantly inhibited the growth of dicotyledonous plants in high concentrations, and was effective as a growth stimulant for single dicotyledonous plants.

Key words: oxygen heterocycles, 2,2-dimethyltetrahydropyran-4-on, 2,2-propagyloxy benzoic acid, single and dicotyledonous plants.

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1. Introduction

Oxygen-containing heterocyclic compounds are widely studied in modern organic and pharmaceutical chemistry, as they form an important basis for drugs, agrochemical agents, and functional materials due to their synthetic flexibility and biological activity [1]. In recent years, special reviews have been published on oxygen-containing heterocycles, discussing recent advances in their innovative synthesis methods and biological applications [2]. 2,2-Dimethyltetrahydropyran-4-one is a six-membered saturated heterocycle. It has two methyl groups in 2,2-dimethyl on one carbon, and a carbonyl group in the 4-position. Due to this, the molecule resembles the structure of a γ -keto ester, which plays an intermediate role in the synthesis of γ -lactones and γ -lactams [3].

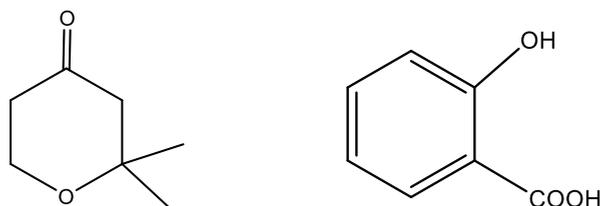
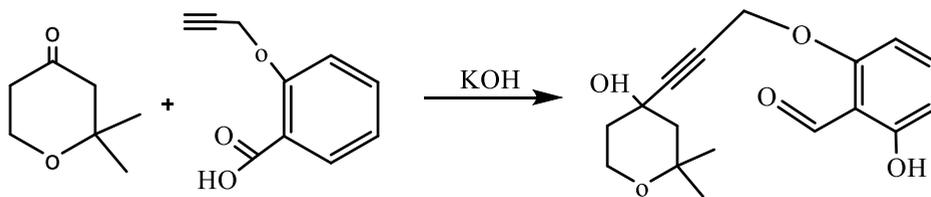


Figure 1 - Structural formula of 2,2-dimethyltetrahydropyran-4-one and salicylic acid.

The propargyl group is widely used in organic synthesis and is an effective reagent for the preparation of complex heterocycles. The introduction of this group is considered an important tool in current research to expand the construction of heterocycles; a review of the synthesis and applications of propargyl derivatives has been published in recent years [3]. In addition, salicylic acid is an important phytohormone in plant physiology, regulating growth and stress responses, its role including the root system and growth [4].



Scheme 1 - Preparation of 2,2-propargyloxybenzoic acid.

Based on these studies, it is clear that new methods for the synthesis of oxygenated heterocycles and the study of their effects on plants are relevant in science and applied chemistry - this demonstrates the integration of modern chemical synthesis and biological testing [5].

2. Experimental part

2.1. Experimental chemical section

The progress of the reactions and the purity of the obtained products were monitored by thin-layer chromatography (TLC) using Sorbifil (Sorbpolymer, Krasnodar, Russia) coated with CTX-1A silica gel, with a UV-254 indicator, particle size 5–17 μm . The eluent for the TLC analysis was a benzene-EtOH mixture in a ratio of 1:3. Solvents for recrystallization and solvents for synthesis were purchased from Merck KGaA with a purity of $\geq 99\%$. Infrared (IR) spectra of the compounds were recorded on a Bruker Avance III 400 MHz spectrometer, on KBr tablets.

The synthesis of 2,2-Propargyloxybenzoic acid was obtained in 72% yield according to the literature [6].

2.2. Experimental biological section

To study the effect of 2,2-propargyloxybenzoic acid on grains, first, homogeneous and clean grains were selected in the experimental work, which were soaked for 24 hours in distilled water or in 2,2-propargyloxybenzoic acid solutions at concentrations of 0.01%, 0.05% and 0.1%; then, the grains were placed in soil or Petri dishes, and their growth was monitored at a temperature of 22–25 $^{\circ}\text{C}$ and a 12-hour light/12-hour dark cycle, and the germination percentage, root and shoot length, number of primary leaves and biomass were measured daily for 48 hours and 60 hours compared with the control group (grains soaked only in distilled water), thus determining the effect of the acid on plant growth [7–10].

3. Results and discussion

In the present study, to determine the effect of 2,2-propargyloxybenzoic acid on grains, grains of monocot and dicot plants were soaked in solutions of different concentrations for 12 hours. *Triticum aestivum* (wheat) was selected as monocot grains, and *Pisum sativum* (pea) as dicot grains. Five concentrations of 2,2-propargyloxybenzoic acid were prepared for the study: 0.1%; 0.01%; 0.001%; 0.0001%; 0.00001%. 25 grains were taken for each experiment, and three replicates were performed for each concentration. *Triticum aestivum* grains soaked in solutions of different concentrations are shown, the number of grains in each beaker is the same, and the concentration of the solution is indicated at the bottom. This figure depicts the initial stage of the experiment, i.e., the process of soaking the grains for 12 hours.



Figure 2 - Appearance of wheat and pea seeds after 12 hours of exposure to 5 different concentrations of 2,2-propargyloxybenzoic acid.

According to the results of the study, the effect of 2,2-propargyloxybenzoic acid varied depending on the plant species and concentration. In all glasses, the pea seeds were wet, and some showed swelling. This is a sign of water absorption and initial physiological activity due to the solution.



Figure 3 - Appearance of wheat and pea seeds placed in a solution of 2,2-propargyloxybenzoic acid after 48 hours.



Figure 4 - Appearance of wheat and pea seeds placed in a solution of 2,2-propargyloxybenzoic acid after 60 hours.

The results of 48 and 60-hour germination of wheat grains showed that 2,2-propargyloxybenzoic acid has a concentration-dependent effect on the initial growth of grains. Compared with the control, changes in the length of roots and shoots were observed in grains treated with acid solutions. At low concentrations (0.001–0.01%), relatively normal development or slight stimulation of shoots was observed, while at high concentrations (0.05–0.1%), a shortening of the root system, poor development of the shoot and general morphological disorders of the shoots were clearly observed.

At high concentrations (0.01% and above), germination was inhibited in most grains, and normal development of the roots and shoots was clearly

observed or they did not appear at all. This indicates that the acid has an inhibitory effect in high doses.

It is observed that the germination process in grains placed in a solution of 2,2-propargyloxybenzoic acid changes in a concentration-dependent manner. In the control (0%) grains, germination signs were weak or not observed at all. At low concentrations (0.0001–0.001%), embryo rupture and the formation of the first radicle were observed in some grains, indicating the beginning of the germination process.

Table 1 – Wheat seeds placed in solutions of different concentrations of 2,2-propargyloxybenzoic acid

Concentration, C (%)	12 h., (cm)	48 h., (cm)	60 h. (cm)
0.1	3.5	7	13.8
0.01	4.5	10	15.5
0.001	2.5	8	10.5
0.0001	4.5	9	16
0.00001	5	10	15.9
Control (water)	4	11	15

Table 2 – Pea seeds placed in solutions of different concentrations of 2,2-propargyloxybenzoic acid

Concentration, C (%)	12 h., (cm)	48 h., (cm)	60 h. (cm)
0.1	1	1.4	1.8
0.01	1	2	2.5
0.001	0.5	0.6	0.7
0.0001	0.4	0.5	0.5
0.00001	0.1	0.4	0.6
Control (water)	0.5	0.5	0.5

The results of the study of the effect of 2,2-propargyloxybenzoic acid showed that this compound acts as a growth stimulant in monocots, but has a negative effect on dicots. As is known, the growth of dicots such as common bean (*Phaseolus vulgaris*) is significantly inhibited at high concentrations, which makes it possible to use 2,2-propargyloxybenzoic acid against weeds. In addition, the effect on the development of fungi in common bean seeds is low, which indicates that this compound has high herbicidal activity and insufficient fungicidal activity, i.e., additional modification is required for its use as a fungicidal agent.

4. Conclusion

The results of the conducted studies showed that the biological activity of 2,2-propargyloxybenzoic acid depends on the plant species. While this compound has a growth-stimulating effect on monocotyledonous plants, it significantly inhibits the growth of dicotyledonous plants, including cowpea, at high concentrations. This property indicates the possibility of using 2,2-propargyloxybenzoic acid as a selective herbicide. In addition, the observation of fungal development on cowpea seeds indicates that the fungicidal activity of this

compound is insufficient and that structural modification or additional studies are necessary for its use as a fungicide.

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ДАРА ЖӘНЕ ҚОС ЖАРНАҚТЫ ӨСІМДІКТЕР ДӘНДЕРІНЕ 2,2-ПРОПАГИЛОКСИ БЕНЗОЙ ҚЫШҚЫЛЫНЫҢ БИОЛОГИЯЛЫҚ ӘСЕРІН БАҒАЛАУ

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Түйіндемe: *Kіріспе.* Оттекті гетероциклді қосылыстар қазіргі органикалық және медициналық химияда маңызды орын алады. Әсіресе тетрагидропиран туындылары олардың құрылымдық әртүрлілігі мен биологиялық белсенділігіне байланысты кеңінен зерттелуде. Осыған байланысты 2,2-диметилтетрагидропиран-4-он мен пропаргилденген салицил қышқылы Фаворский реакциясы арқылы оттекті туынды — пропаргилоксибензой қышқылын алып оны дара және қос жарнақты өсімдіктер дәндерінде биологиялық белсенділігін анықтау агробиология мен фитохимияның өзекті мәселе болып табылады. Жұмыстың *мақсаты мен міндеттері* 2,2-диметилтетрагидропиран-4-он мен пропаргилденген салицил қышқылы негізінде оттекті гетероциклді қосылысты синтездеп, дара және қос жарнақты өсімдік дәндеріне биологиялық белсенділігін зерттеу. *Міндеттері* бастапқы қосылысты Принс реакциясы арқылы алу, Фаворский реакциясы көмегімен жаңа туынды синтездеу және биологиялық белсенділігін зерттеу. *Қорытынды (тұжырымдар).* Оттекті гетероцикл 2,2-диметилтетрагидропиран-4-он диметилвинил-этинилкарбинолмен күкірт қышқылы ортасында және сынап сульфатын катализатор ретінде қолдану арқылы, Принс реакция механизмі арқылы 70 % шығыммен алынды. Алынған 2,2-диметилтетрагидропиран-4-онды Фаворский реакциясы арқылы салицил қышқылының ацетиленді туындысымен әрекеттестіру арқылы 2,2-диметилтетрагидропиран-4-онның ацетиленді туындысы 2,2-пропагилокси бензой қышқылы 57 % шығыммен синтезделді. Алынған оттекті гетероцикл қосылыстардың физико-химиялық қасиеттері анықталды және ИҚ спектроскопиясымен зерттелді. 2,2-пропагилокси бензой қышқылының дара және қос жарнақты өсімдік дәндеріне жүргізілген биологиялық белсенділігін зерттеу нәтижелері бойынша қос жарнақты өсімдіктердің өсуін жоғары концентрацияларда айтарлықтай тежеді, ал дара жарнақты өсімдіктерге өсу стимуляторы ретінде ықпалды екені анықталды.

Түйінді сөздер: оттекті гетероциклдер, 2,2-диметилтетрагидропиран-4-он, 2,2-пропагилокси бензой қышқылы, дара және қос жарнақты өсімдіктер

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ОЦЕНКА БИОЛОГИЧЕСКОГО ВОЗДЕЙСТВИЯ 2,2-ПРОПАРГИЛОКСИ БЕНЗОЙНОЙ КИСЛОТЫ НА СЕМЕНА ОДНОДОЛЬНЫХ И ДВУДОЛЬНЫХ РАСТЕНИЙ

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Резюме. *Введение.* Кислородсодержащие гетероциклические соединения занимают важное место в современной органической и медицинской химии. Особое внимание уделяется производным тетрагидропирана, которые широко исследуются благодаря их структурному разнообразию и биологической активности. В связи с этим получение кислородсодержащего производного — пропаргилоксибензойной кислоты — из 2,2-диметилтетрагидропиран-4-она и пропаргилированной салициловой кислоты с использованием реакции Фаворского, а также определение его биологической активности на семенах однодольных и двудольных растений является актуальной задачей агробиологии и фитохимии. *Цель и задачи работы.* Целью работы является синтез кислородсодержащего гетероциклического соединения на основе 2,2-диметилтетрагидропиран-4-она и пропаргилированной салициловой кислоты, а также изучение его биологической активности на семенах однодольных и двудольных растений. *В задачи исследования* входили получение исходного соединения с применением реакции Принса, синтез нового производного с помощью реакции Фаворского и исследование его биологической активности. *Заключение (выводы).* Кислородсодержащий гетероцикл 2,2-диметилтетрагидропиран-4-он был получен с выходом 70 % при взаимодействии диметилвинилэтинилкарбинола в среде серной кислоты с использованием сульфата ртути в качестве катализатора по механизму реакции Принса. В результате взаимодействия полученного 2,2-диметилтетрагидропиран-4-она с ацетиленовым производным салициловой кислоты в условиях реакции Фаворского было синтезировано ацетиленовое производное — 2,2-пропаргилоксибензойная кислота — с выходом 57 %. Были определены физико-химические свойства полученных кислородсодержащих гетероциклических соединений и проведены их исследования методом ИК-спектроскопии. По результатам изучения биологической активности 2,2-пропаргилоксибензойной кислоты установлено, что при высоких концентрациях она существенно ингибирует рост двудольных растений, тогда как в отношении однодольных растений проявляет стимулирующее действие.

Ключевые слова: кислородсодержащие гетероциклы, 2,2-диметилтетрагидропиран-4-он, 2,2-пропаргилоксибензойная кислота, однодольные и двудольные растения.

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