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ACETYLATION OF HERACLEUM SOSNOWSKYI MANDEN AS A LOCAL CONTROL METHOD TO PREVENT ITS EXPANSION

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Abstract. *The article proposes the way to control aggressive invasive plant Heracleum sosnowskyi Manden. This method excludes contact of the plant dangerous sap with human skin, and based on injecting of 6% apple vinegar in optimal volumes into the stems of the plant before its fructification. Injection of apple vinegar into the hollow part of the stems causes complete necrosis of the aerial part of the plant within 48 hours. At the same time, aceylation is an exclusively selective process characteristic for Heracleum sosnowskyi Manden only. This reaction does not have the negative environmental effects observed when using glyphosate, imidazolinine, sulfonylurea, and other herbicides. The article confirms the exceptional selectivity of injections on Heracleum sosnowskyi Manden. According to the research, the injections of 6% apple vinegar do not affect on the hollow stems of Sónchus oleráceus. Indeed, the injections of water into the stems of both types of plants under study do not cause the death of their aerial parts. Moreover, the high-performance liquid chromatography of stems after injections with 6% apple vinegar shows an induced increase in the content of furanocoumarins in 48 hours as a response to an irritant dangerous to the plant. Moreover, the content of xanthotoxin increased by 1.7 times.*

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Introduction

The extensive mass media propaganda concerning with the exceptional danger of *Heraculum sosnowskyi Manden* based on scientific research and real results forms an opinion of the need for total destruction of this plant. Mechanical destruction of *Heracleum sosnowskyi Manden* includes slanting of aerial parts of the plant up to three times per season, from April to September [1]. When slanting, the sap containing furanocoumarins fall on the skin and can cause painful photo-burns from any source of ultraviolet radiation [2]. When burning thickets of *Heracleum sosnowskyi Manden* there are problems related to prolonged smouldering of this plant, and its failure to maintain an open flame when burning [3, 4]. This plant is considered to have no natural pests, and the role of moth caterpillars and elephant beetle larvae is not significant in controlling the plant expansion [5]. Herbicidal treatment is effective and environmentally justified only in places remote from human activity. Its treatment with herbicides based on glyphosate, imidazolinine, and sulfonylurea near the railway track stops the plant growth and expansion; ensures the safety of railway transport [6]. The chemical effect of herbicides, in the cases specified in [7], provides for their integral effect - the treatment of the entire plant landscape in a particular territory. Indeed, all known methods of *Heracleum sosnowskyi Manden* control require considerable labor, and the results are not immediately obvious. The absence of federal laws on the organization of this invasive plant control causes non-uniform *Heracleum sosnowskyi Manden* destroying [8]. Meanwhile, in Europe and North America this kind of activity slightly decreased [16, 17]. Mainly, there is monitoring of its expansion through the aerial photography.

The development and implementation of "green" chemical technologies for the production and use of valuable and useful substances extracted from *Heracleum sosnowskyi Manden* are under-invested. This article presents the results of point or differentiated chemical treatment of *Heracleum sosnowskyi Manden* by injection with 6% apple vinegar. However, this method minimizes labour costs, eliminates contact with the poisonous sap of the plant under study, and protect the growing plant landscape intact.

Main body

The choice of 6% apple vinegar as a tool in the *Heracleum sosnowskyi Manden* control is not accidental. The peoples of the Caucasus still pickle the stems of this plant and use them for food; 6% red grape vinegar is used for pickling [9]. Therefore, it is of particular interest to make contact of this plant with acetic acid (acetylation) in the natural conditions of its growth in Russia. Point or differentiated chemical treatment of *Heracleum sosnowskyi Manden* was reduced to injection with a medical syringe with 6% apple vinegar into the hollow stems of the plant. In early works, the resistance of *Heracleum sosnowskyi Manden* to sodium chlorate [10] and electrolysis products of aqueous solutions of NaCl was studied [11].

The picking of the original and processed with 6% apple vinegar according to GOST 32097-2013 [12] *Heracleum sosnowskyi Manden* was provided on the territory of the Yaroslavl municipal district (Karabikhskoye rural settlement 57°53′55″5 north latitude and 39°76′74″2 east longitude) during the last decade of July. The stems were processed both before the formation of inflorescences and after the flowering of the plant. Stems were taken from the selected plant with a height of no more than 110 cm before treatment (initial), and after necrosis of the aerial parts of the plant after injection with a medical syringe with 6% apple vinegar. To confirm the selective effect of vinegar on *Heracleum sosnowskyi Manden*, comparative injections into this plant with water for injection of FS 2.2.0019.18 were performed. The selectivity of the 6% apple vinegar action *on Heracleum sosnowskyi Manden* only was tested in compare with the garden wasp *Sónchus olecàceus*, which was also injected with 6% apple vinegar and water similar to *Heracleum sosnowskyi Manden*.

Table 1 presents data on the effect of the 6% apple vinegar injection volume on the rate of necrosis of the *Heracleum sosnowskyi Manden* aerial parts.

By Table 1, any volume of injections in the selected range from 2.5 to 30.0 ml causes a necrosis of the aerial parts of *Heracleum sosnowskyi Manden*, namely stems before the formation of inflorescences and stems after flowering.

Table 1. The effect of the 6% apple vinegar injection volume on the necrosis rate of the *Heracleum sosnowskyi Manden* aerial parts

Quantity of plants	Injection volume, ml	Necrosis rate, h		
		24	36	48
Stems of *Heracleum sosnowskyi Manden* before the formation of inflorescences				
15	2.5	46,7%	60%	100%
15	5.0	80%	100%	-
15	7.5	86,7%	100%	-
15	10.0	100%	-	-
10	20.0	100%	-	-
10	30.0	100%	-	-
Stems of *Heracleum sosnowskyi Manden* after flowering				
10	2.5	70%	100%	-
10	5.0	90%	100%	-
10	10.0	100%	-	-
10	20.0	100%	-	-

With an increase in the volume of injections (starting from 10 ml of 6% apple vinegar), necrosis occurs in 24 hours. The rate of necrosis was assessed by the time the plant completely fell to the soil and its leaves color changing and drying.

Fig. 1 shows photos of the plants under study before (*a*) and after injections (*b*) with 6% apple vinegar in a volume of 2.5 ml within 48 hours.

(*a*) (*b*)

Fig. 1. Photos of the plants under study before (*a*) and after (*b*) injections of 6% apple vinegar in a volume of 2.5 ml within 48 hours

We pick shoots from the plant shown in Fig. 1, *a*. They were picked for 1 hour before processing with vinegar, crushed in a RHB-2944 blender, and their sap was pressed out on a cast–iron press (juicer) Juicer Machine. However, we pick the shoots of *Heracleum sosnowskyi Manden* within 48 hours after injections with 6% apple vinegar (see Fig. 1, *b*). Notable, it was impossible to obtain sap from the leaves subjected to necrosis. We press sap according to the technology described above.

Also, we subject the sap to chloroform extraction to obtain furanocoumarins, which can cause photochemical burns of the skin [13].

Moreover, we extract the sap twice with constant stirring on a UED-10 magnetic stirrer for 24 hours at a temperature of (25±3) ˚C. We separate the organic phase with furanocoumarins on a dividing funnel and dried under vacuum on a rotary evaporator at a temperature of 50 ˚C.

Then, we wash the 300 ml of dry residue off with a solution of 10% NaOH under heating in a water bath to (65±5) ˚C, and extract furanocoumarins on a separation funnel with 100 ml chloroform portions four times; combine the chloroform extracts, add 200 ml of 5% sodium carbonate, mix them intensively for 10 minutes, separate the organic phase again using a separation funnel, and dried it with anhydrous sodium sulfate within 24 hours [14].

Then, we wash the 300 ml of dry residue off with a solution of 10% NaOH in under heating in a water bath to (65±5) ˚C, and extract furanocoumarins on a separation funnel with 100 mL chloroform portions four times; distil chloroform off on a rotary evaporator, add 30 ml of acetonitrile, treat with ultrasound for 5 minutes, and filter it on a Nylon membrane filter with a pore diameter of 0.45 microns. Meanwhile, we use the filtrate as a test solution for high-performance liquid chromatography (HPLC).

Chromatography conditions:

- Welch Xtimate C18 150*4.6 mm, 3 microns column;
- mixture of water and acetonitrile in a ratio of 60:40 was used as the mobile phase. The flow rate was maintained at 1000.00 µL/min;
- detection was performed by a spectrophotometric detector at a wavelength of 250 nm using the Multichrome program. The sample volume is 20 µl. The analysis time is 20 minutes.

Fig. 2 shows a chromatogram of furanocoumarins extracted from the sap of *Heracleum sosnowskyi Manden* before injection with apple vinegar.

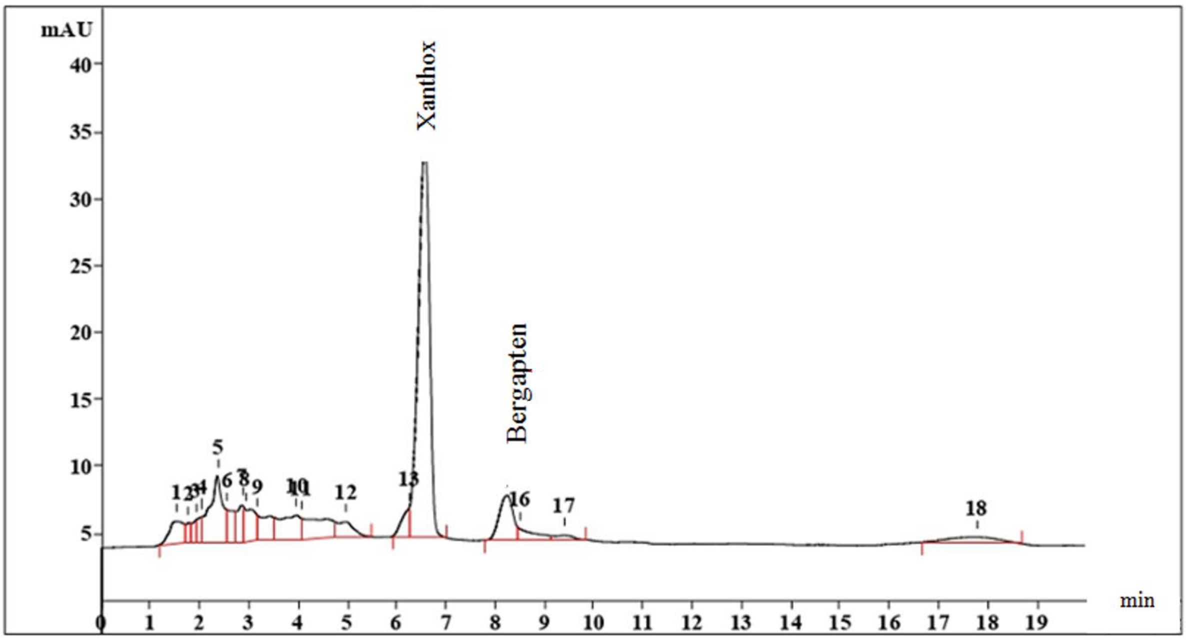


Fig. 2. Chromatogram of furanocoumarins extracted from the sap of *Heracleum sosnowskyi Manden* before injection with 6% apple vinegar

The chromatogram has 18 peaks, of which four are characteristic of linear and angular shapes of furanocoumarin molecules. The major peaks are those characterizing linear furanocoumarins (Fig. 3): xanthoxin and bergapten (Table 2), which exhibit stronger photosensitizing effects compared to furanocoumarins having angular shapes of molecules (Fig. 4), the phototoxic effect of which is noticeably weaker (peak 5 for angelicin, peak 9 for sphondyl) [18].

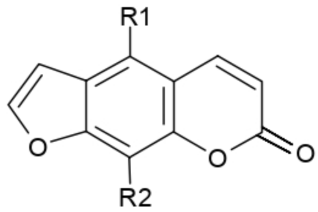
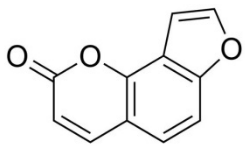


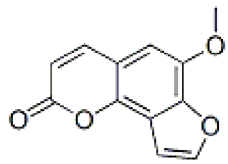
Fig. 3. The structure of major linear forms of furanokoumarins *Heraculum sosnowsky Manden*

Table 2. Substituents of the *Heracleum sosnowskyi Manden* major linear furanocoumarins

Title	R1	R2
Xanthoxin	H	$-OCH_3$
Bergapten	$-OCH_3$	H



(A) angelicin



(A) angelicin

Fig. 4. The structure of the *Heraculum sosnowsky Manden*major linear forms of furanokoumarins

After injections with 6% apple vinegar in 48 hours, the chromatogram of furanocoumarins presented in Fig. 5 changed. Due to the response of *Heraculum sosnowsky Manden* to an external chemical stimulus, there is an induced increase in the content of xanthoxin in the sap by 1.7 times. It leads to necrosis of the aerial parts of the plant from the phototoxic effect due to an excess of furanocoumarins. Xanthoxin causes oxidative stress. Oxidative stress reflects an imbalance between the reactive oxygen species in the plant and the ability of the biological system to clean itself of reaction intermediates and repair the damage caused. Violation of the cells redox status causes toxic consequences through the production of peroxides and free radicals, which damage all cells components, including proteins, lipids, and DNA. During oxidative metabolism, an oxidative stress causes chemical damage and ruptures DNA strands [19]. The oxidative stress caused by xanthoxin starts a regulated process of programmed cell death, cellular apoptosis, as a result of which the cell breaks up into separate apoptotic bodies limited by the plasma membrane.

For verification of major chromatogram peaks affiliation to xanthotoxin and bergapten, chromatograms of the pharmaceutical product "Ammifurin" Pharmcentre VILAR ZAO (Russia) were obtained. They presented in Fig. 6.

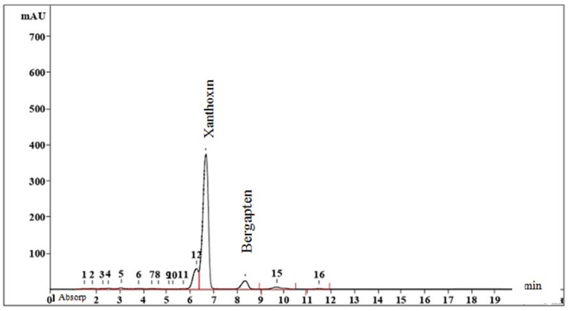


Fig. 5. Chromatogram of furanokoumarins extracted from the *Heraculum sosnowsky Manden* sap after injections with 6% apple vinegar within 48 hours

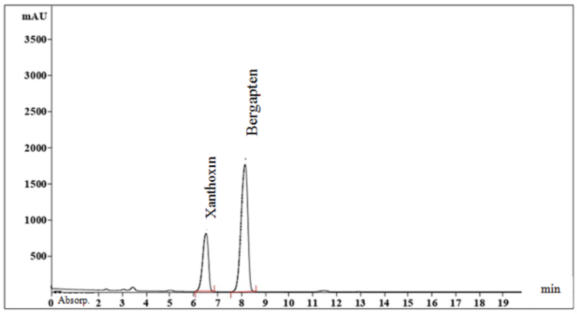


Fig. 6. Chromatogram of furanocoumarins extracted from the pharmaceutical product "Ammifurin" Farmcenter VILAR ZAO (Russia)

Table 3 presents the results of calculations of the chromatographic peaks areas of xanthotoxin and bergapten from the substances under study.

Table 3. Results of calculations of chromatographic peak areas of xanthotoxin and berkapten (in %) from the substances under study

Substance	Furanokumarin		Total peak area, %
	Xanthotoxin	Bergapten	
Pharmaceutical product Ammifurin	28.23	71.77	100
Sap of *Heracleum sosnowskyi Manden* before injections	45.17	6.05	51.22
Sap of *Heracleum sosnowskyi Manden* after injections with 6% apple vinegar	76.83	5.41	82.24

To confirm the results obtained, experiments were conducted on water injections into hollow stems of *Heraculum sosnowskyi Manden* and *Sónchus oleráceus.* Injections were external mechanical stimuli for plants. As a result of these injections, none of the plants underwent necrosis of the aerial parts (Table 4) within 48 hours or more.

Table 4. The effect of the injections composition on the necrosis rate of the plants aerial parts

Sample size	Injection volume, ml		Necrosis rate, h		
	6% apple vinegar	Water for injection	24	36	48
Stems *of Heraculum sosnowskyi Manden* before the formation of inflorescences					
15	-	2.5	-	-	-
15	-	5.0	-	-	-
15	-	10.0	-	-	-
15	-	20.0	-	-	-
Stems of *Sónchus oleráceus*					
10	2.5	-	-	-	-
10	5.0	-	-	-	-
10	10	-	-	-	-
10	20	-	-	-	-
15	-	5.0	-	-	-
15	-	10.0	-	-	-
15	-	20.0	-	-	-

The injections of 6% apple vinegar into the stems of *Sónchus oleráceus*, which sap does not contain furanocoumarins [15], in the studied volume range did not cause a necrosis of the aerial parts of the plants under study.

Conclusion

Therefore, injections of 6% apple vinegar (acetylation) in volumes from 2.5 to 30.0 ml into the stems of *Heraculum sosnowskyi Manden* before its fruiting cause necrosis of the plants aerial parts within 24-48 hours. The cause of necrosis is an induced increase in the content of linear furanocoumarins due to the response of *Heraculum sosnowskyi Manden* to an external chemical stimulus. Injections with 6% apple vinegar resulted in a 1.7-fold increase in the xanthoxin content of the plant sap as determined by HPLC, causes a necrosis of the plant from phototoxic effects due to the excess of this furanocoumarin. The proposed method of control *Heraculum sosnowskyi Manden* excludes human contact with the dangerous sap of this plant released during mechanical slanting. In general, the method is based on point contact of a chemical irritant with the plant through injections, eliminating contamination with herbicides of large areas of natural landscapes during their spraying.

Hence, acetylation is an exclusively selective process, characteristic for *Heraculum sosnowskyi Manden* only. According to our research, injections of 6% apple vinegar are inactive on the hollow stems of *Sónchus oleraceus*. Indeed, the injections of water into the stems of both types of plants under study do not cause their aerial parts plant failure.

This method of control allows us to remove *Heraculum sosnowskyi Manden* locally (differentially) from natural landscapes without disturbing the growth of other decorative and/or harmless plant species. With the massive overgrowth *of Heraculum sosnowskyi Manden*, it is necessary to use well-known integrated methods of control. It can provide for multiple mechanical slanting of its shoots over a vast territory, one-time treatment with gentle herbicides, agrotechnical processing of the soil, etc. [1].

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