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FEATURES OF EXTRACTING OF HERACLEUM SOSNOWSKY FRUITS

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This paper deals with the using of Sosnowsky hogweed processing products in the chemical industry. Essential oils containing carboxylic acid esters are the most valuable important components obtained after fruits oil extraction of the studied plant. The extraction was carried out in a Soxlet apparatus sequentially with light petroleum ether, an equal volume mixture of benzene and acetone and isopropanol. The resulting essential oil was used to prepare a compound with vaseline oil to make rubber. The use of Sosnowsky hogweed essential oils in the formula of rubber makes it possible to extend the temperature range of their use at low temperatures. The recycling of rubber containing essential oils into crumb rubber will enable it to be used in road pavements and eliminate the problem of them cracking in winter time. The recycling of rubber containing essential oils into crumb rubber allows us to use it for road surface and to eliminate the problem of winter time cracking.

Introduction

Every year, the invasive plant *Heracleum Sosnowskyi Manden*, or Sosnowsky hogweed, occupies up to 10% of the arable land in Europe [1, 2-4]. This plant can cause photochemical burns in human when contact with the skin, thus making it a potential hazard to the public [5].

Nowadays, the issue of limiting the spread of this invasive plant is decided privately by the land owner.

In the places where this plant can pose a potential threat to human health (city parks, adjacent to railways lands, and non-agricultural lands) the overgrowth of this plant is treated with strong, continuous-type herbicide "Tornado" based on glyphosate [6], which effects on the environment and can have a negative impact on human health.

On small and medium-sized agricultural lands Sosnovsky's hogweed is removed during the cultivation. In the most of the large wastelands, restrictive measures against the spread of Sosnowsky's hogweed are neither applied nor envisaged.

Limiting the spread of this plant can be achieved through the use of herbicides and by targeted, integrated processing into products required by society.

Study

The hogweed burgeon contains up to 17–31% wt. sugar [7] and was predicted as one of the promising and economically raw for biofuel production. By the monitoring of sap sugar content at different stages of plant vegetation in 2019-2020, it was observed [8] that the maximum sap sugar content was 7.5% wt. and occurred during budding and flowering period. But bioethanol could not be obtained in relevant quantities from the sugar sap of the stems of Sosnowsky hogweed by the digestion of *Saccharomyces cerevisiae*. The substances in the juice inhibited the biological processes of sugar digestion and exhibited antimycotic properties [9]. Infrared spectra of sugar and sugar concentrate obtained from Sosnowsky hogweed were made by IR-Fourier RX-1 of "Perkin Elmer" spectrophotometer.

The sugar concentrate obtained from the sap by evaporation, as confirmed by infrared spectroscopy data (Fig. 1), is using for wood-peel pellets production as a binder and flavoring agent for the resulting pellet fuel [10].

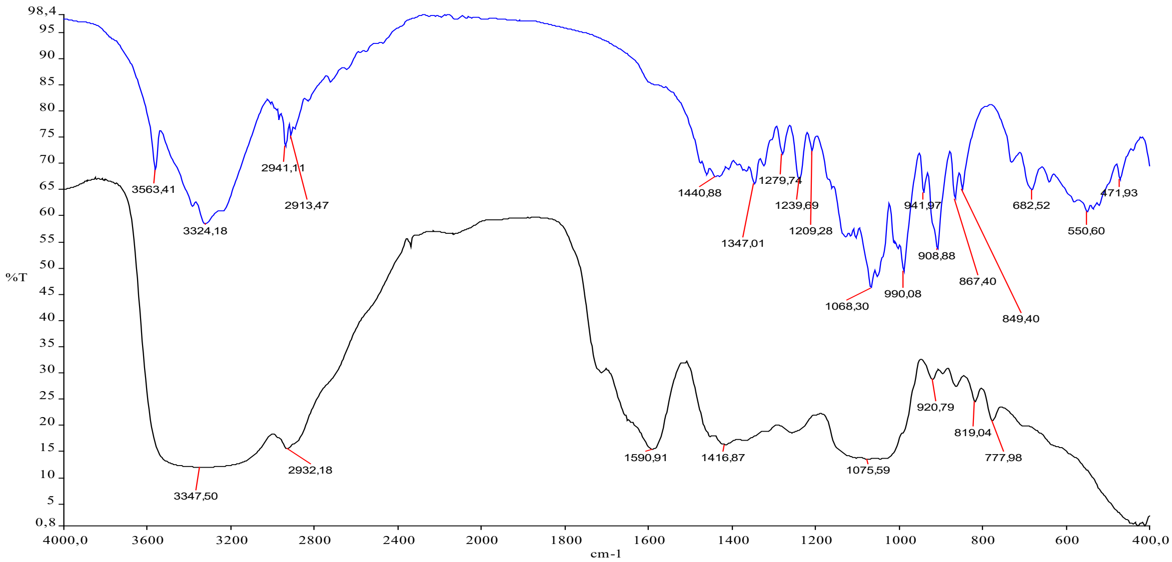

Fig. 1. IR spectra of sugar (bottom graph) and sugar concentrate from Sosnowsky hogweed (top graph)

The IR spectra of sugar concentrate and sugar (a disaccharide consisting of α-glucose and β-fructose) show absorption bands of 844 and 891 cm^{-1}, are typical for glucosides and polysaccharides, and absorption bands of 1070 cm^{-1} are typical for fructose. The presence of a broad absorption band of 3200–3600 cm^{-1} in both spectra indicates the presence of hydroxide groups bound together by hydrogen bonds in the disaccharides.

According to [11], *Heracleum Sosnowskyi Manden* fruits contain 1–10% essential oils. By GOST 31791-2017 "Essential oils and floral and herbal essential oils" these fruits cannot be used in perfumery, cosmetics and food industries or in medicine, but they can be successfully used in chemical technology, in particular for technical rubber production.

The higher frost resistance of technical rubbers may be the result of the high content of carboxylic acid esters [12] of the ester oil.

Fruits of Sosnovsky's hogweed were seeded at noon in cloudy weather and in the absence of precipitation in the period 15.08.2020 – 25.08.2020 in a floodplain meadow with coordinates: 57.717644 north latitude and 39.829009 east longitude, Yaroslavl, Russia. After mechanically removing the fruit from the umbels, the seeds were dried out of sunlight, packed in sealed cardboard boxes and stored in a cool dry place.

The essential oil was extracted from air-dry raw material one month and one year after seeding by light petroleum ether extraction in a Soxhlet apparatus and by 3-step sequential extraction method "light petroleum ether - mixture of acetone and benzene (1:1 by volume) - isopropanol" year later.

The chemical composition of essential oils was analyzed using a gas chromatograph with a DB-624 capillary column with a stationary phase of 6%, cyanopropylene phenyl 94% and a film thickness of 2.5 micrometers, 30 m length, 0.53 mm diameter, equipped with a flame ionization detector, an electronic integrator Crystallux 4000M.

We raised the column temperature from 60 °C to 200 °C at a heating rate of 4 °C/min and controlled for 2.5 min, then raised to 250 °C at a heating rate of 20 °C/min and controlled for 5 min. Medium gas: hydrogen. Column flow rate: 3.0 ml/min; injector temperature: 250 °C; detector temperature: 290 °C; flow division: 1:5; hydrogen flow rate: 30 ml/min; air flow rate: 300 ml/min.

The components were identified by their retention times. The quantitative content of the components was determined by internal rationing.

Analysis of a chromatogram of the essential oil obtained one month after its extraction shows that the essential oil contains 36 components (Table 1), of which 13 have been identified, mass content in the essential oil exceeds 1.0% (major components). The yield of the essential oil extracted with petroleum ether from the fruit of *Heracleum Sosnowskyi Manden* was 3.4% wt.

Table 1. Quantitative composition of major components of Sosnowsky hogweed fruit essential oil one month (2020) and one year (2021) after seeding.

No.	Component	Ingredient weight in essential oil, %	
		2021	2020
1	1-Hexanol	-	1.057
2	Terpene	9.523	14.671
3	Octanal	3.626	5.225
4	Hexylacetate	1.957	3.297
5	Octanol	2.927	3.257
6	Hexylisobutyrate	2.776	2.313
7	Hexylbutyrate	7.727	6.891
8	Octylacetate	25.630	27.575
9	Hexylisovalerate	2.540	2.581
10	Octilisobutyrate	1.607	2.324
11	Hexylcapronate	4.190	3.375
12	Octilisovalerat	11.562	7.568
13	Octylcapronate	1.877	1.449
14-36	Other	24.088	18.417

Table 1 shows the total amount of identified carboxylic acid esters in the essential oil is 57.5% wt., of which 27.6% wt. is octyl acetate. These results are correlating with the results of tests of essential oils [13].

Chromatographic analyses show the essential oil content of Sosnowsky hogweed fruit declines to trace levels after a one-year storage cycle, and it is a significant problem for the industrial year-round production of essential oils by extraction.

By Table 1, reanalysis of the essential oil after one year shows a quantitative decrease of terpenes, octanal, hexylacetate, octylisobutyrate and a complete absence of 1-hexanol and there is an increase in hexylbutyrate, hexylcapronate, octylisobutyrate and total unidentified components of the essential oil. The total amount of carboxylic acid esters identified increased by 2.3%.

When light petroleum ether was extracted in a Soxhlet apparatus with air-dry raw material from the fruit of Sosnowsky hogweed, stored for one year, no essential oil could be quantitatively obtained. We found only trace amounts of the components making up the essential oil. Further extraction of raw material with acetone and benzene mixture (1:1 by volume) allowed to extract additionally 12.071% wt. 1-hexanol, 1.073% wt. octylacetate and 3.243% wt. hexylisovalerate at total mass yield of 3.2%, the final extraction with isopropyl alcohol did not increase of carboxylic acid esters content of the extract.

The essential oil of Sosnowsky hogweed fruit has a nice fruity smell, typical for the carboxylic acid esters. But this oil has low processability. To improve processability of essential oil in the manufacture of rubber compound, a compound of vaseline oil with essential oil in a 1:1 ratio (vegetable oil) by volume, from which the fraction with a boiling point below 85 °C was completely removed. When making the compound with petroleum jelly medical oil the processability is increased, but the organoleptic properties are greatly reduced and the compound began to smell bad.

The kinematic viscosity of the compounds was determined with a capillary viscometer VPZH-1 according to GOST 33-2000.

Rubber mixtures based on light crepe with a compound of vaseline oil and essential oil in the ratio of 1:1 (vegetable oil) by volume and I-12A oil (industrial oil) were made on heating rollers PD-320 160/160 with friction of the rollers 1:1,08 during 15 minutes.

The methods of definition of premature vulcanization ability of rubber compounds samples according to GOST 10722-76 (ST SEV 3662-88), methods of definition of rubber compounds vulcanization characteristics according to GOST 12535-84 (ST SEV 3813-82) with use of vibroreometer "Monsanto" were used, methods for determination of elastic tensile strength properties of rubber compounds according to GOST 270-75 using ITS 8220-10 tensile breaking machine, method for determination of frost resistance of rubber compounds according to GOST 408-78.

Table 2 shows the technological characteristics of vaseline oil compounds with essential oil.

Table 2. Technological characteristics of Vaseline oil compounds with essential oils of Sosnowsky hogweed fruits

Indicator name	Essential oil content, % vol.				
	0	10	25	50	75
Refractive index, n_D^{20}	1.4721	1.4661	1.4633	1.4557	-
Density at 20 °C, g/cm^3	0.8502	0.8373	0.8122	0.8204	0.8316
Kinematic viscosity, mm^2/sec: at 20 °C	126.76	42.40	19.31	20.09	22.53
at 40 °C	56.61	25.52	11.10	10.21	15.87
at 50 °C	32.08	14.76	8.44	8.10	13.41
Self-ignition temperature, °C	290	270	265	260	235

According to Table 2, a compound of vaseline oil with essential oil in a ratio of 1:1 by volume has optimum processing characteristics. At this oil ratio, the kinematic viscosity values in the temperature range under study are extremely reduced at the maximum permissible essential oil content of the compound.

Table 3 presents the comparative properties of rubber compound and technical rubber based on light crepe containing industrial oil I-12 and a compound of vaseline oil with Sosnowsky hogweed extracts.

Table 3. Comparative properties of rubber compound and technical rubber based on light crepe containing industrial oil I-12 and a compound of vaseline oil with with Sosnowsky hogweed extracts

Recipe and indicator name	Oil, wt. h.	
	Industrial I-12 (5,00)	Plant (5,00)
Sulphur	2.00	2.00
Mercaptobenzthiazole	0.65	0.65
Tetramethylthiuramdisulphide	0.30	0.30
Zinc oxide	15.00	15.00
Stearic acid	2.00	2.00
Vulcanizing ability of the rubber compound at 120 °C		
$M_{\min}$, units. Mooney	9	16
t_5, min	17	7.5
t_{35}, min	20	15
Δt_S, min	3	7.5
Rheometer characteristics of the rubber compound at 151 °C		
M_L, H·m	4.6	6.4
t_s, min	2.9	1.3
M_H, H·m	21.5	23.1
ΔM, H·m	16.9	16.7
t_{50}, min	5.5	3.0
t_{90}, min	5.8	3.8
t_r, min	40.0	-
R_V, min^{-1}	34.8	40.7
Rubber properties (vulcanization mode in an electric curing press 151 °C x 15 min)		
f_p, MPa	24.0	24.4
ε_p, %	930	950
θ, %	9.6	6.7
Frost resistance coefficient at minus 45°C	0.72	0.89

Conventions

$M_{\min}$ - minimum viscosity (torque) at 120 °C;

t_5 - the time from the start of the test when the viscosity of the rubber mixture exceeds the minimum viscosity $M_{\min}$ by 5 units at 120 °C;

t_{35} - the time from the start of the test when the viscosity of the rubber mixture exceeds the minimum viscosity $M_{\min}$ by 35 units at 120 °C;

M_L - minimum torque;

t_S - start time of curing at given temperature;

M_H - minimum torque;

ΔM - difference between the maximum and minimum torque;

t_{50} - time to reach 50% degree of cure at given temperature;

t_{90} - the time to reach the optimum curing time at given temperature;

t_r - reversion time;

R_V - measure of the rate of curing;

f_p - conditional tensile strength;

ε_p - relative elongation at break;

θ - relative residual elongation.

The technical rubber comparative properties (Table 3) show that the introduction of vegetable oil into the rubber mixture slightly increased its tendency to subvulcanize to compare with industrial oil but there is no overvulcanization of the rubber mixture sample with vegetable oil.

Rubber containing vegetable oil has the value of coefficient of cold-resistance at minus 45 °C by 23% more in comparison to rubber plasticized with industrial oil with practically the same level of deformation strength properties under uniaxial tension.

The increased frost resistance of containing vegetable oil rubber isexplained by the presence of 57.5% wt. of carboxylic acid esters in the essential oil of Sosnowsky hogweed fruit. In this regard, essential oil as a component of rubber compounds is not only a softener like industrial oil I-12A, but also a plasticizer of rubbers. It allows to recycle these rubbers into rubber crumb as a component of production of polymer-bitumen binders [14, 15], reducing of road surfaces cracking at low temperature.

Conclusions and recommendations

1. The essential oil of Sosnowsky hogweed can be used as a plasticizer of technical rubbers to increase their frost resistance.
2. The essential oil content of Sosnowsky hogweed fruit declines to trace levels after a one-year storage cycle, and it is a significant problem for the industrial year-round production of essential oils by extraction.

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References

1. **Betekhtina A.A., Rozhnina D.A., Ivanova L.A., Malygin M.V., Ivanov L.A.** Relative growth rate and its components in invasive species heracleum Sosnowskyi and congeneric native species H. Sibiricum. *Rossijskij zhurnal biologicheskih invazij.* 2018. N 4. P. 7-16 (in Russian)
2. **Kondratyev M.N., Budarin S.N., Larikova Y.S.** Physiological and ecological mechanisms of invasive penetration of Sosnowskyi hogweed (heracleum Sosnowskyi Manden in exploitable agroecosystems. *Izvestiya of Timiryazev Agricultural Academy*. 2015. V. 2. P. 36-49 (in Russian)
3. **Nielsen, C., H.P. Ravn, W. Nentwig and M. Wade (eds.)** The Giant Hogweed Best Practice Manual. Guidelines for the management and control of an invasive weed in Europe. Forest & Landscape Denmark, Hoersholm,, 2005. 44 p.
4. **Lutyńska R.** Studies on the acclimatization of Heracleum sosnowskyi Manden and its use as a fodder plant. *Biuletyn Instytutu Hodowli I Aklimatyzacji Roślin*. 1980. N 139. P. 3-36.
5. **Pesnya D.S., Serov D.A., Vakorin S.A., Prokhorova I.M**. Research of the toxic, mitosis modifying and mutagen effect of Heracleum sosnowsky. *Yaroslavskij pedagogicheskij vestnik*. 2011. N 4. V. III, (Natural Sciences). P. 93-98 (in Russian)
6. **Miroshnikova D.I., Kiryushin V.A., Motalova T.V.** About application of glyphosate based herbicides. *Science to the Young (Eruditio Juvenium)*. 2018. N 2. URL: https://cyberleninka.ru/article/n/voprosy-primeneniya-gerbitsidov-na-osnove-glifosata (accessed 24.05.2021). (in Russian)

7. **Dorzhiev S.S., Pateeva I.B**. Energy-saving technology for obtaining bioethanol from the green mass of plants of the genus Heraculum. *Polzunovskiy Vestnik.* 2011. N 2/2. P. 251-255 (in Russian)
8. **Golovkov A.E., Vahromeeva O.V., Pavlov A.V., Solov'ev V.V.** Monitoring of the sugar content of Sosnovsky hogweed at different stages of the plant's vegetation. *Sem'desyat tret'ya vserossijskaya nauchno-tekhnicheskaya konferenciya studentov, magistrantov i aspirantov vysshih uchebnyh zavedenij s mezhdunarodnym uchastiem. 20 aprelya 2020 g., YAroslavl': sb. materialov konf. V 2 ch. CH.* [Elektronnyj resurs]. Yaros lavl': Izd-vo YAGTU, 2020. P. 164-166. 1 opt. disk (in Russian)
9. **Tkachenko K.G., Preobrazhenskaya N.E., Sacyperova I.F.** Antimicrobial effect of essential oils of some types of Heraculum L. *Rastitelnye Resursy*. 1988. 24(1). P. 99-104. (in Russian)
10. **Baranova N.D., Pavlov A.V**. Investigation of the properties of wood-petiole pellets. *Sem'desyat tret'ya vseros – sijskaya nauchno-tekhnicheskaya konferenciya studentov, magistrantov I aspirantov vysshih uchebnyh zavedenij s mezhdunarodnym uchastiem. 20 aprelya 2020 g., YAroslavl': sb. Materialov konf. V 2 ch. CH. 1* [Elektronnyj resurs]. YAroslavl': Izd-vo YAGTU, 2020. P. 252-256. 1 opt. disk (in Russian)
11. **Tkachenko K.G.** Essential oils of Heracleum Ponticum (Lipsky) Schischk and H. Sosnowskyi Manden fruits. *Nauchnye vedomosti. Ser. estest. nauk. Bel.GU.* 2010. N 3(74). V. 10. P. 23-27 (in Russian)
12. **Чайкун А.М., Елисеев О.А., Наумов И.С., Венедиктов М.А.** Compouding principles in the field of frost-resistant rubbers. *Aviacionnye Materialy and Technologii.* 2013. N 3. P. 53-55 (in Russian)
13. **Tkachenko K.G., Zenkevich I.G.** The composition of essential oils from the fruits of some species of Heraculum L. *Rastitelnye Resursy.* 1987. 23(1). P. 87-91 (in Russian)
14. **Vysockaya M.A., Kuznecov D.A., Litovchenko D.P., Barkovskij D.V. Shiryaev A.O.** The need for a plasticizer in the production of polymeric - bitumen binders. *Vestnik BGTU im. V.G. SHuhova.* 2019. N 5. P. 16-22. DOI: 10/ 34031/article_5cd6df466bb9e0.32764094 (in Russian)
15. **Airey G.D.** Factors affecting the rheology of polymer modified bitumen. Polymer Modified bitumen. Woodhead Publishing Cambridge, UK, 2011. P. 238-263.

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