

TOXIC INFLUENCE OF NEW WOOD PRESERVATIVES ON PLANTS GROWTH

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TOKSYCZNY WPŁYW NOWYCH ŚRODKÓW OCHRONY DREWNA NA WZROST ROŚLIN

Badano toksyczny wpływ dwóch nowych chlorków imidazoliowych na rośliny: dwuliścienną *Sinapis alba* Linnaeus i jednoliścienną *Hordeum vulgare* Linnaeus. Związki te uznano za nowe środki ochrony drewna z uwagi na ich znakomite własności grzybobójcze. Stwierdzono, że są one mniej toksyczne dla jęczmienia niż dla gorczycy. Chlorek 3,3'-[(2,7-dioksyoktymetyleno) bis (chlorek 1-oktyloimidazoliowy)] był mniej fitotoksyczny dla obu roślin niż chlorek 1-decylo-3-heksylotiometyloimidazoliowy.

S u m m a r y

Toxic influence of two new imidazolium chlorides was examined on plants: dicotyledonous *Sinapis alba* Linnaeus and monocotyledonous *Hordeum vulgare* Linnaeus. These compounds are meant to be new wood preservatives because of their excellent fungicidal properties. They were proved to be less toxic to barley than to charlock. The compound 3,3'-[(2,7-dioxyoktymethylene) bis (1-oktyl)imidazolium] chloride was less fitotoxic to both plants than 1-decyl-3-hexylotiomethylimidazolium chloride.

INTRODUCTION

Quaternary ammonium salts are new generation of agents preserving wood from rotting. They substituted traditional preservatives (arsenic, copper and chromium salts), which were withdrawn from market because of their toxicity to warmblooded organisms and the danger associated with exploited impregnated wood inactivation. Very precious group of ammonium salts are imidazolium derivatives having great fungicidal potential. They are toxic to *Basidiomycotina* (basidiomycete) fungi that attack wood of foliose species as well as coniferous species. Moreover, these compounds are selective depending on the kind of substituent in imidazolium ring and preserve both types of wood from different species of fungi. Fungicides on the basis of imidazolium substituted with alkyl chains of different length are optimal biocides against *Coniophora puteana*, fungus causing brown decay of coniferous species wood. On the other hand, imidazolium salts substituted with alkyl chains

of approximate length are best to preserve foliose species wood from white decay, caused by fungus *Trametes versicolor*. Because of the above mentioned properties they are used especially for preserving wood exposed to moistening, for example in interior woodwork, chimneys, cross-ties, shingles and fences [2, 6, 8].

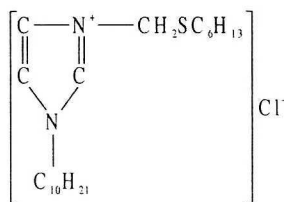
These agents may endanger the environment during their application and while using and degrading the preserved wood. Throughout utilizing the preserved timber the agents may leach into soil during rainfalls. Accumulated in soil they will influence the soil microflora and plants. Two new compounds having good fungicidal properties were examined [7]. Their influence on root and stem growth of *Sinapis alba* Linnaeus and *Hordeum vulgare* Linnaeus was determined. The plants were chosen on the basis of OECD [4].

MATERIALS AND METHOD

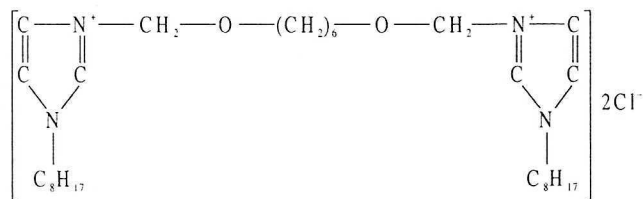
Two quaternary ammonium salts were chosen for the experiment:

- 1-decyl-3-hexylotiomethylimidazolium chloride (DHTMIC)
- 3,3'-(2,7-dioxyoktymethy) bis (1-oktyl)imidazolium chloride] (DOOMIC)

First compound, DHTMIC, with molecular formula of $C_{20}H_{39}N_2SCl$ has a molecular weight of 371.45 (Fig. 1). The content of active substance is 96.8 %.



1-decyl-3-hexylotiomethylimidazolium chloride (DHTMIC)



3,3'-(2,7-dioxyoktymethy) bis (1-oktyl)imidazolium chloride] (DOOMIC)

Figure 1. Structural formulae of examined compounds

Second compound, DOOMIC, with molecular formula of $C_{30}H_{56}N_4O_2Cl$ has a molecular weight of 574.90 and active substance content of 98% (Fig. 1). Both substances are chemical individuals, readily water-soluble in examined concentrations.

The test was conducted according to the method described in Polish Standard [5]. Cylindrical vessels, 8x11 cm, with perforated bottoms were used. Seeds of *Sinapis alba* Linnaeus and *Hordeum vulgare* Linnaeus used in the test were not seasoned. The ves-

sels were filled with sand of a low sorption capacity. Water retention capacity of the ground, determined by means of balance-drier, was 17.3%. The sand had been dried in the temperature of $60 \pm 5^\circ\text{C}$, till air-dry state and then the vessels were filled to the height of about 9 cm. Each vessel contained about 0.5 kg of sand. Contaminant series of DHTMIC and DOOMIC comprised the following concentrations: 1 mg/kg, 3 mg/kg, 9 mg/kg, 27 mg/kg and 81 mg/kg; 60 cm³ of tested compound solution was poured into each vessel. It provided 70% of the previously determined water holding capacity. This amount of liquid ensured its uniform distribution in the whole sand volume and prevented the solution from the loses caused by leaching. Five germinated barley or charlock seeds having roots from 2 to 5 mm long were placed in each vessel on the depth of 10 mm. The seeds had been germinating for 48 hours on Petri dishes in an incubator at the temperature of 20°C.

The planted vessels were put into a growth chamber and incubated for 5 days. Days were 10 hours long and nights – 14 hours. Day temperature was $23 \pm 1^\circ\text{C}$; night temperature – $20 \pm 1^\circ\text{C}$. Each test concentration as well as the control without examined compounds were assayed in two replicates.

After set time of experiment the length of root and stem was measured. The concentration causing the 50% growth inhibition with reference to the control was taken as a measure of the toxic influence of the compounds.

RESULTS AND DISCUSSION

The studies showed varied influence of tested compounds on plants. The results proved that broad-leaved plants are more sensitive to imidazolium chlorides than corn. IC₅₀ values for barley's root growth were from 10 to 250 times higher than for charlock (Fig. 2) and accounted for 630.0 and 2587.6 mg/kg for DHTMIC and DOOMIC, respectively (Tab. 1). This suggests tested wood preservatives use as efficient pesticides. Their use in agriculture would enable effective raising crops protection from weeds.

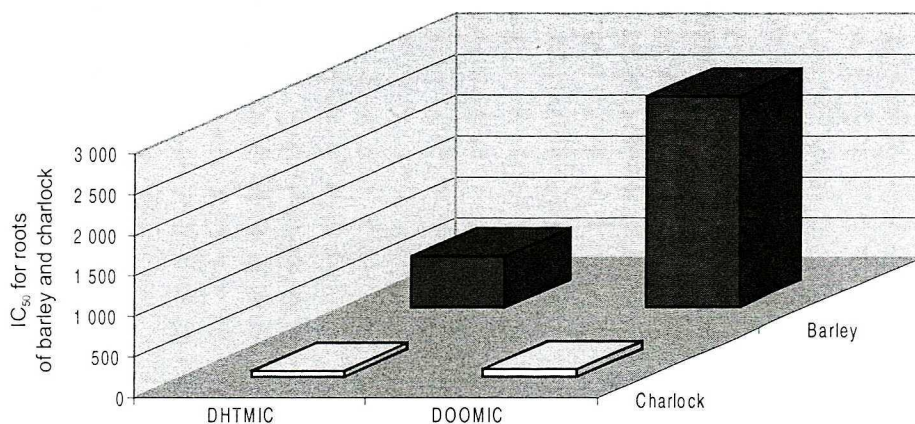


Figure 2. DHTMIC and DOOMIC influence on barley and charlock roots growth

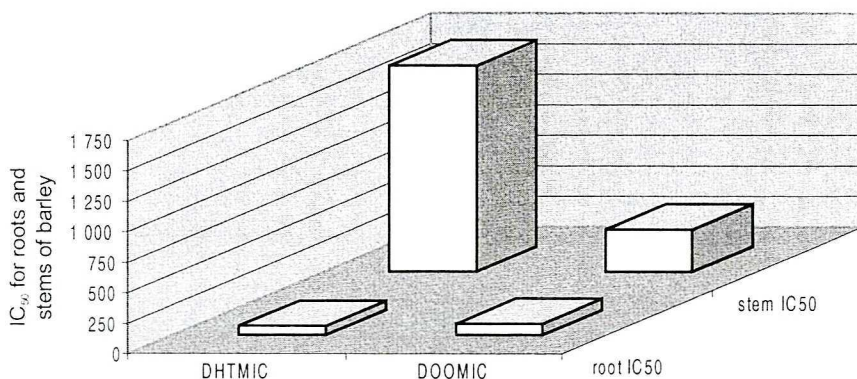
Table 1. IC₅₀ values for tested plants species

Compound	DHTMIC				DOOMIC			
	Root growth	SD	Stem growth	SD	Root growth	SD	Stem growth	SD
Tested plant	IC ₅₀		IC ₅₀		IC ₅₀		IC ₅₀	
Barley	630.00	0.7	ND		2 587.60	2.0	ND	
Charlock	75.00	0.1	1 685.60	0.5	94.40	0.3	345.80	0.4

SD – standard deviation

ND – no data

It was also proved that both compounds inhibit the root growth stronger than the stem growth (Fig. 3, Tab. 1). This relation was observed for dicotyledonous as well as monocotyledonous plants. It is a consequence of the fact that roots take polar compounds (tested agents) more readily than stems [10]. Moreover, quaternary ammonium compounds disturb amino – acids transport [3, 9]. It was found that charlock roots are from 4 to 22 times more sensitive to imidazolium chlorides than its stems. That is why residuals accumulated in soil may be harmful to cultivated plants. It is dangerous especially in dry lands due to slow degradation of the compounds as well as in sandy soils with low sorption capacity.

Figure 3. IC₅₀ values for roots and stems growth of barley

It was also proved that concentrations of these compounds ranging from 1 to 9 mg/kg caused barley stem growth stimulation of about 15% (Fig. 4). The most probable cause of stimulation was the fact that quaternary ammonium salts have ability to disturb amino – acids transport, what may decrease their levels in roots and increase in stems [3]. For this reason stimulation of the stem growth and root growth inhibition may occur at the same time.

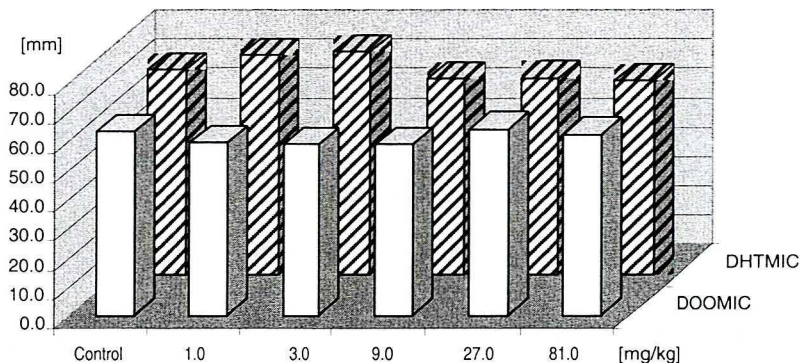


Figure 4. Comparison of DHTMIC and DOOMIC influence on barley stem growth

It was also found that DOOMIC (compound with higher molecular weight) was less toxic for both plants than DHTMIC (Fig. 2, Tab. 1). The most probable reason of this phenomenon is different molecular weight of tested wood preservatives. Its influence was confirmed by studies conducted by Ernst [1], who proved cationic surfactants toxicity to be the smaller, the higher was the molecular weight. On the other hand, greater toxicity of DHTMIC is surely the result of sulfur presence in its molecule.

CONCLUSIONS

The experiment proved toxic influence of tested new wood preservatives on dicotyledonous plant charlock *Sinapis alba*. Determined IC_{50} values of charlock root growth inhibition were 75.00 and 94.41 mg/kg for DHTMIC and DOOMIC, respectively. Stronger inhibition of root growth in comparison to stem growth was observed (Tab. 1). Barley *Hordeum vulgare* appeared to be less sensitive to imidazolium chlorides. The compound 3,3'-[(2,7-dioxyoktymety) bis (1-oktyl) imidazolium chloride] (DOOMIC) indicated lower toxicity against both tested plants than 1-decyl-3-hexylotiomethylimidazolium chloride (DHTMIC).

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REFERENCES

- [1] Ernst R., J. Arditti, P.L. Healey: *Biological effects of surfactants I. Influence on the growth of orchid seedlings*, New Phytol., **70**, 457 (1971).
- [2] Fojutowski A.: *Wartość grzybobójcza i wymywalność chlorku alkilodimetylobenzyloamoniowego w metodzie agarowo – klockowej*, [in:] Materiały Sympozjum: Czwartorzędowe sole amoniowe i obszary ich zastosowania w gospodarce, Poznań 1997, 103–113.
- [3] Horowitz M., A. Givelberg: *Toxic Effects of Surfactants Applied to Plant Roots*, Pestic. Sci. **10**, Society of Chemical Industry, 547–557 (1979).

- [4] *OECD Guidelines for the Testing of Chemicals*, Guideline 208 Part 1, Paris, France 1993.
- [5] PN – ISO 11269 – 1, Jakość gleby, *Oznaczanie wpływu zanieczyszczeń na florę glebową*.
- [6] Urbanik E., J. Zabielska-Matejuk: *New quaternary ammonium chlorides for wood preservation*, [in:] *Prace Instytutu Technologii Drewna*, Issue 1/2, Poznań 1996, 3–9.
- [7] Urbanik E., J. Zabielska-Matejuk, J. Pernak: *Antifungal properties of new imidazolium chlorides against *Coniophora puteana*, *Trametes versicolor*, *Chaetomium gloeosporium**, *Material und Organismen*, **31**, 247 (1997).
- [8] Urbanik E., J. Zabielska-Matejuk, J. Pernak: *Quaternary ammonium compounds for wood preservation*, IV International Symposium Chemistry Forum, Warsaw 1998, 111.
- [9] Witek S.: *Biologiczna aktywność czwartorzędowych soli amoniowych i lizosomotropowych amin*, [in:] *Materiały Sympozjum: Czwartorzędowe sole amoniowe i obszary ich zastosowania w gospodarce*, Poznań 1998, 9–20.
- [10] Żurawska M., J. Glabiszewski, H. Żurawski: *Wpływ różnych dawek 2,4-D na siewki pomidorów i mikroflorę glebową w doświadczeniach testowych*, [in:] *Materiały pokonferencyjne „Bioindykacja Skażeń Przemysłowych i rolniczych” PAN*, Wrocław 1983, 210–213.

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