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# From research on the use of chiral ionic liquids with a natural origin substituent for wood protection

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**Abstract:** *From research on the use of chiral ionic liquids with a natural origin substituent for wood protection.* Antifungal activities of chiral ionic liquids - menthoxymethylimidazolium derivates against brown-rot decay fungus (*Coniophora puteana*), white-rot decay fungus (*Trametes versicolor*) and blue-stain fungus (*Sclerophoma pithyophila*) were determined using screening agar-plate and agar-block methods. Results from antifungal tests revealed that 1-hexyl-3-[(*1R,2S,5R*)-(-)menthoxymethyl]imidazolium chloride exhibited the strongest antifungal activity against wood decay fungi (*basidomycetes*) compared with the commercial didecyldimethylammonium chloride. Whereas compound with twelve carbons alkyl substituent has a weak antifungal activity. The infrared spectral analysis (FTIR ATR) confirmed that chiral imidazolium ionic liquids were built into the structure of the treated wood.

*Keywords*: chiral ionic liquids, fungi, penetration, protection

## INTRODUCTION

Biologically active substances of natural origin, occur in nature, which can be easily obtained and then converted to compounds with defined properties are the subject of research of many scientists. Menthol is an organic compound obtained from peppermint and other mint oils or it's produced synthetically. Most commonly naturally encountered is the (-)-menthol, with assignet configuration (*1R,2S,5R*). It exhibits the strongest biological activity. In medicine, natural menthol is used as an antiseptic. Matan at al. (2009) describes the average resistance of menthol against white-rot fungal and weak activity against mould.

Our interest was in chiral ionic liquids obtained from natural (*1R,2S,5R*)-(-)-menthol. Some of the obtained compounds exhibit an anti-static and anti-microbial properties on a higher level than benzalkonium chloride (Feder-Kubis 2011). The new chiral imidazolium ionic liquids with the substituent of (*1R,2S,5R*)-(-)-menthol characterize an effective antibacterial activity (Pernak et al. 2007). So far the antifungal activity of the interesting compounds to the wood rotting fungi has not been described.

Optimization of the structure of compound required beyond the determination of the toxicity research of the impact onto wood. In this article the results of laboratory tests of activity against fungi and bonding of menthoxymethylimidazolium salts with the Scots pine wood *Pinus sylvestris* L. has been described.

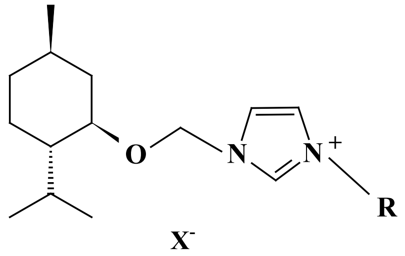
## MATERIALS AND METHODS

### Fungal strains

The following species of test fungi were selected for investigations: *Coniophora puteana* (Schum.: Fr.) Karst. Strain BAM 15, *Trametes versicolor* (L.:Fr.) Pilát strain CTB 863A, *Sclerophoma pithyophila* (Corda) van Höhn strain S 231.

**Chemicals**

In the presented paper a new chiral quaternary imidazolium salts with the (*1R,2S,5R*)-(-) menthoxymethyl substituent was studied. The structures of compounds are presented below:



R= $CH_3$, $C_2H_5$, $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$, $C_7H_{15}$, $C_8H_{17}$, $C_9H_{19}$, $C_{12}H_{25}$, (*1R,2S,5R*)-(-)-menthoxymethyl
$X^-$ = chloride, nitrate

Structures of compounds was confirmed performing $^1$H NMR and $^{13}$C NMR spectra with the Varian Model XL 300 spectrometer.

**Determination of fungicidal activity**

**Screening agar-plate method**

The fungicidal effectiveness was determined using the method described by Ważny and Thorton (1986). The fungal growth rates were measured in 90-mm-diameter dishes using the agar-dilution test. The results were used to calculate the effective dose ($ED_{50}$, $ED_{100}$: concentrations retarding the fungal growth rate by 50 or 100%, respectively, in comparison with plates where the toxicant was omitted) and the lethal dose (LD: concentrations causing death of inoculums). Didecyldimethylammonium chloride, a commercially available fungicide, was used as a reference compound.

**Agar – block method**

The fungicidals activity of studied ionic liquids was determined on Scots pine (*Pinus sylvestris* L.) wood using standardized method according to screening agar-block method described by Zabielska-Matejuk (1997). Scots pine sapwood wood samples after drying at 102±2°C, were saturated under vacuum conditions with solutions of studied ionic liquids. All samples were placed in Kolle flasks and subjected to *C. puteana* and *T. versicolor* fungi. The flasks were incubated at 22±1°C and 70 ±5% relative humidity. Wood samples were plain cleaned of mycelium, dried at 102 ±2°C and weighed. Weight losses were determined in accordance with the procedures of the standards PN-EN 113: 2000/A1:2005.

**Determination of penetration depth**

Samples of Scots pine (*Pinus sylvestris* L.) sapwood were used, at a density of 480-540 kg $m^{-3}$ measuring 50 x 50 x 20 mm and conditioned to a moisture content of 12 ±1%, according of the PN-C-04901:2014-09. On the 50 x 50 $mm^2$ wood surface 0.5 g of investigated salts were applied. Then, the samples were conditioned in the dishes over a saturated solution of ammonium nitrate at 20 ±2°C for 7 days. Subsequently, the samples were cut perpendicularly to fibers by means of a cross cut saw, and were sprayed carefully on the cross-section surface with bromophenol blue indicators (giving a typical blue color on contact with ionic liquid). The range of blue section were marked with a sharp pencil, which permitted determination of the penetration depth of ionic liquid.

**FTIR ATR analysis**

To identify the binding of chiral ionic liquids with Scots pine (*Pinus sylvestris* L.) wood was used analysis of the infrared spectra obtained of internal reflection ATR technique. For the ATR analysis the veneer of pine sapwood (approx. 0.5 mm thick) were impregnated with solutions of ionic liquids, using of vacuum-pressure method, applying -88 kPa pressure for 30 min and atmospheric pressure for 60 min, and dried at room temperature. Spectroscopic studies were performed on the device IFS 66 V / S Bruker. Reflectance spectra were registered in the mid-infrared range 4000 - 400 $cm^{-1}$ with resolution of 2 $cm^{-1}$.

RESULTS

The $ED_{50}$, $ED_{100}$, LD values determined for menthoxymethylimidazolium derivates are presented in Table 1-2. Effective doses of examined salts against test fungi depend on the length of alkyl substituent. 1-hexyl-3-[(*1R,2S,5R*)-(-)-menthoxymethylimidazolium chloride and nitrate proved more effective against *C. puteana* and *T. versicolor* than commercial didecyldimethylammonium chloride.

Table 1. Effective (ED) and lethal (LD) doses of examined 1-alkyl-3-[(*1R,2S,5R*)-(-)-menthoxymethyl]imidazolium chlorides

| Ionic liquids | R | *Coniophora puteana* | | | *Trametes versicolor* | | | *Sclerophoma pithyophila* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $ED_{50}$ | $ED_{100}$ | LD | $ED_{50}$ | $ED_{100}$ | LD | $ED_{50}$ | $ED_{100}$ | LD |
| | | ppm | | | | | | | | |
| A | $CH_3$ | 1000 | 2500 | 2500 | 1000 | 2500 | 2500 | 750 | 1000 | 5000 |
| B | $C_4H_9$ | 500 | 750 | 750 | 250 | 500 | 1000 | 250 | 750 | 2500 |
| M1 | $C_5H_{11}$ | 250 | 750 | 2500 | 100 | 250 | 500 | 250 | 500 | 750 |
| M2 | $C_6H_{13}$ | 250 | 250 | 1000 | 50 | 100 | 250 | 250 | 250 | 500 |
| M3 | $C_8H_{17}$ | 100 | 1000 | 2500 | 25 | 500 | 750 | 100 | 750 | 750 |
| C | $C_9H_{19}$ | 100 | 2500 | 5000 | 50 | 1000 | 5000 | 100 | 1000 | 2500 |
| D | $C_{12}H_{25}$ | 750 | >5000 | >5000 | 50 | >5000 | >5000 | 100 | 5000 | >5000 |
| E | menthol | 250 | 1000 | 1000 | 25 | 1000 | 2500 | 100 | 250 | >5000 |
| Didecyldimethyl-ammonium chloride | | 25 | 1000 | 1000 | 50 | 1000 | 2500 | 25 | 100 | 250 |

Table 2. Effective (ED) and lethal (LD) doses of examined 1-alkyl-3-[(*1R,2S,5R*)-(-)-menthoxymethyl] imidazolium nitrates

| Ionic liquids | R | *Coniophora puteana* | | | *Trametes versicolor* | | | *Sclerophoma pithyophila* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $ED_{50}$ | $ED_{100}$ | LD | $ED_{50}$ | $ED_{100}$ | LD | $ED_{50}$ | $ED_{100}$ | LD |
| | | ppm | | | | | | | | |
| N1 | $CH_3$ | 1000 | 2500 | 2500 | 2500 | 2500 | 2500 | 50 | 5000 | 5000 |
| N2 | $C_2H_5$ | 1000 | 2500 | 2500 | 1000 | 2500 | 2500 | 500 | 2500 | 2500 |
| N3 | $C_4H_9$ | 500 | 750 | 750 | 250 | 750 | 1000 | 500 | 1000 | 2500 |
| N4 | $C_6H_{13}$ | 250 | 250 | 500 | 50 | 250 | 500 | 250 | 500 | 500 |
| N5 | $C_7H_{15}$ | 100 | 500 | 750 | 50 | 250 | 500 | 250 | 500 | 500 |

The new chiral mentoxymenthylimidazolium compounds are very active in the prevention of coniferous and broadleaved wood biodegradability (table 3). Fungicidal values of this compound with butyl and penthyl substituents for *C. puteana* (pine) were from 1.67 to 2.8 kg/m$^3$, for *T. versicolor* (beech) were at the level of 4.3 – 6.6 kg/m$^3$. Similar results were obtained for the ionic liquids with the two (*1R,2S,5R*)-(-)-menthoxymethyl substituents.

Table 3. Fungicidal values of examined 1-alkyl-3-[(*1R,2S,5R*)-(-)-menthoxymethyl]imidazolium chlorides against *basidiomycetes*

| Ionic liquid | Species of wood / Fungus species | Impregnation solution concentration [%] | Mass loss [%] | | Fungicidal value according to PN-EN 113 [kg m$^{-3}$] |
|---|---|---|---|---|---|
| | | | Treated wood | Control wood | |
| M1 | Scots pine / *Coniophora puteana* | 0.25 -0.4 | 0.7 | 48.7 | 1.79 - 2.85 |
| M2 | | 0.4-0.63 | 0.0 | 29.8 | 2.76 - 4.39 |
| M3 | | 0.4-0.63 | 0.6 | 42.1 | 2.87 - 4.47 |
| B | | 0.25-0.4 | 2.3 | 52.6 | 1.67 - 2.80 |
| E | | 0.25-0.4 | 0.6 | 19.59 | 1.82 - 2.91 |
| M1 | Beech/ *Trametes versicolor* | 0.63 - 1.0 | 2.0 | 12.3 | 4.36 - 6.63 |
| M2 | | 0.63 - 1.0 | 0.4 | 13.9 | 4.37 - 7.08 |
| M3 | | 0.63 - 1.0 | 1.6 | 14.0 | 4.42 - 7.05 |
| B | | 0.63 - 1.0 | 0.3 | 13.5 | 4.40 - 7.03 |

Penetration depth of new chiral ionic liquids onto the Scots pine sapwood was of 3.2 mm, which is comparable to the penetration of NaF.

Comparison of ATR spectra of control Scots pine wood treated with wood spectra with 1-butyl-3-[(*1R,2S,5R*)-(-)- menthoxymethyl]imidazolium chloride (B) (Fig.1) shows the spectral changes of the material evidence of treated with this compounds. The most visible changes in the spectrum of spectral pine + compound (B) increase in the intensity of bands respectively at: 2921 and 2851 cm$^{-1}$ can be included. The bands at 2921 and 2851 cm$^{-1}$ come from vibrations respectively ν (C-H) and asymmetric ν (C-H) symmetrical-$CH_2$-groups of the aliphatic chain (butyl) introduced into the wood structure cation. Evidence for introducing the cation into the wood structure is also an increase in the intensity of the band at 1467 cm$^{-1}$ assigned to the vibration δ (C-H) of asymmetric from groups-$CH_3$ and-$CH_2$-chain aliphatic. Creation of the bands (increase in absorption) in the band of torsional and fan vibrations γ (C-H) of methylene groups -$CH_2$- located at the 1103 cm$^{-1}$ confirms the incorporation of the alkyl substituent cation. These changes indicate the bonding of 1-butyl-3-[(*1R,2S,5R*)-(-)-menthoxymethyl]imidazolium chloride with pine wood.

## CONCLUSIONS

Inhibition of coniferous and broadleaved wood biodegradation by new menthoxymethylimidazolium ionic liquids depend on the cation structure of these compounds. The infrared spectral analysis (FTIR-ATR) confirmed that chiral imidazolium ionic liquids were built into the structure of the treated wood. The observed spectroscopic changes in the ATR spectrum are a proof that chiral ionic liquids cation with the menthol was fixed in the wood structure.

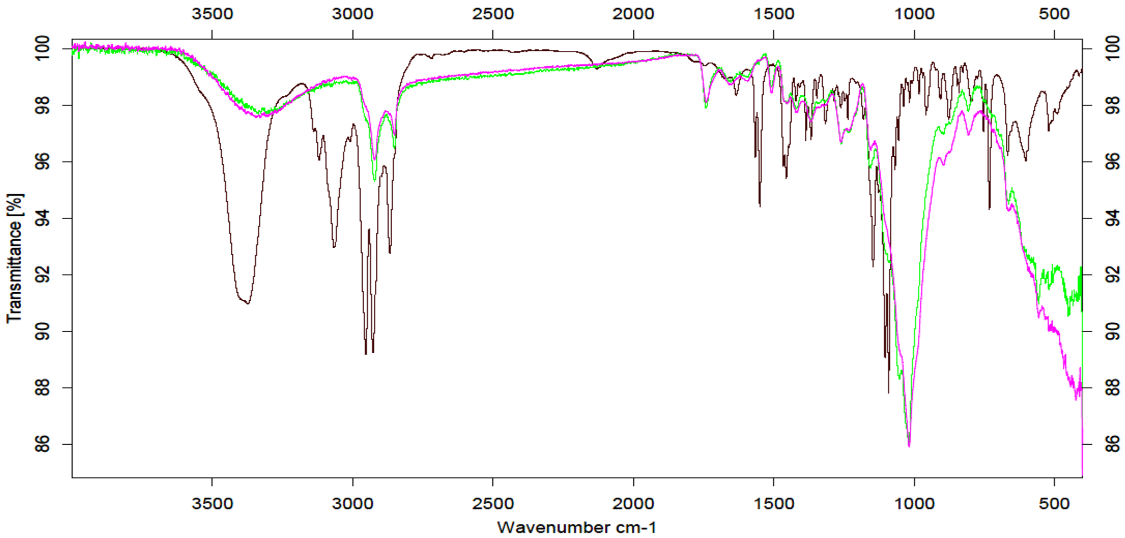


Figure 1. ATR spectra of Scots pine wood: control wood – pink, treated with 1-butyl-3-[(*1R,2S,5R*)-(-)-mentoxymethyl]imidazolium chloride (B) – green, compound (B) – brown

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**Streszczenie**: *Z badań nad wykorzystaniem chiralnych cieczy jonowych z podstawnikiem pochodzenia naturalnego do ochrony drewna.* Badano metodą agarowo-płytkową i agarowo-klockową aktywność przeciwgrzybową chiralnych cieczy jonowych, pochodnych mentoksymetyloimidazolu, wobec grzybów rozkładu brunatnego, białego oraz wywołującego siniznę drewna. Chlorek 1-heksylo-3-[(*1R,2S,5R*)-(-) -mentoksymetylo]imidazoliowy wykazał najsilniejsze działanie przeciwgrzybowe wobec *basidiomycetes*, porównywalne do komercyjnego chlorku didecylodimetyloamoniowego. Analiza spektralna FTIR ATR potwierdziła wbudowanie chiralnych cieczy jonowych w strukturę nasyconego drewna sosny *Pinus sylvestris* L..



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