Dicationic triazolium fungicidal ionic liquids with herbicidal properties

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Abstract

The purpose of the present study was to synthesize the dicationic ionic liquids exhibiting herbicidal and fungicidal activities. A homologue series of ten dicationic ionic liquids was synthesized using commercial triazole fungicide (tebuconazole) and evaluated in terms of their possible antifungal and herbicidal activities. Dicationic triazolium compounds containing different linkers were prepared via acid–base reaction between the corresponding dicationic hydroxides and herbicides in the form of free acids. Additionally, the ionic liquids were fully characterized using NMR and thermal analysis. The herbicidal efficacy was tested during greenhouse experiments, using lambsquarters and oilseed rape as the test plants. In the case of determination of antifungal activity, six fungal species were used: *Sclerotinia sclerotiorum*, *Botrytis cinerea*, *Fusarium culmorum*, *Fusarium oxysporum*, *Colletotrichum* sp. and *Monographella nivalis*. The obtained results indicate that the conversion of compounds into dicationic ionic liquids affects their fungicidal and herbicidal activity. In the case of tests carried out on fungi, no difference in activity was observed at higher doses, except *Monographella nivalis*. However, at lower concentration (10 ppm), there is a reduction in efficacy compared to the reference substance. In addition, all obtained compounds are characterized by high activity.

Keywords Herbicide · Fungicide · Dicationic ionic liquid · Herbicidal ionic liquid

Introduction

Ionic liquids (ILs) are a vast group of chemical compounds characterized by a melting point below 100 °C. The notable trait of ionic liquids is their ionic structure and the fact that they are considered as “designer” compounds. The selection of ions allows to control the physical, chemical and biological properties. One of the main classifications of ILs includes their three generations (Hough et al. 2007). The 1st generation comprises ionic ILs which exhibit unique physical properties. ILs characterized by additionally determined chemical properties are described as the second generation, whereas the third generation is characterized by targeted

biological properties. The last generation is of high significance due to the potential application of commercial and broadly used organic compounds (such as pharmaceuticals or pesticides), which are well studied in terms of properties, including their toxicity towards warm-blooded organisms and the natural environment (Bica and Rogers 2010; Shamshina et al. 2015).

The detailed review of pesticides, especially in EU, prevents and restricts the use of numerous efficient active compounds which have been employed for years. The design of ILs which comprise the commonly used compounds in the form of a cation or anion may be a cheap and efficient method. This allows to obtain new compounds as ILs with altered properties and retained efficiency of action of the substrate.

Herbicidal ionic liquids (HILs) are currently an alternative to commonly available pesticides and are defined as ILs containing at least one herbicidal ion (Pernak et al. 2011). They are safe due to their limited volatility in relation to, e.g., formulations containing an ester of a herbicidal acid (Cojocar et al. 2013). In addition, they are characterized by the ease to regulate the toxicity of the preparation and allow to obtain preferred physiochemical properties by

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selection of appropriate counter-ion (Kordala-Markiewicz et al. 2014; Niemczak et al. 2019). The discovery of HILs in 2011 showed that it was possible to obtain a new type of more biologically active and potent herbicides based on different organic acids (Pernak et al. 2014a, b; Niemczak et al. 2017; Tang et al. 2018; Wang et al. 2019; Ding et al. 2014; Zhu et al. 2015). However, it is also possible to prepare salts which consist of a cation manifesting herbicidal activity (Piotrowska et al. 2016).

Novel types of dual functional salts include ILs which exhibit biological activity. Introduction of another functional counterion allows to obtain salts with additional properties (Lewandowski et al. 2014). It is possible to synthesize HILs with a cation used as a plant growth regulator or fungicide and an anion manifesting high herbicidal activity (Pernak et al. 2013, 2014a, b). In addition, bifunctional ILs derived from the plant resistance inducer BTH can be applied as a new type of a pesticide with antibacterial properties (Śmiglak et al. 2014, 2016).

Dicationic ionic liquids (DILs) comprise two identical or different monocations linked together by a rigid or flexible organic spacer and paired with two singly charged anions (Bhatt et al. 2015; Moumene et al. 2015; Al-Mohammed et al. 2015; Niu et al. 2018). Recently, DILs comprising imidazolium, ammonium, pyridinium, and phosphonium cations or their combinations to form asymmetric salts have been developed and extensively studied (Sahu et al. 2014; Yonekura and Grinstaff 2014). Important advantages of DILs in comparison to monocationic ILs include high thermal and chemical stability, larger liquid ranges, higher solubility of compounds, surface properties, and lower volatility (Chinnappan et al. 2015; Fareghi-Alamdari et al. 2016; Serva et al. 2016).

Triazoles are compounds consisting of a five-membered ring with three nitrogen atoms located at the 1, 2, 3 or 1, 2, 4 positions (Mehrkesh and Karunanithi 2013). Compounds containing the triazole group have found application as drugs which exhibit various biological activities, such as antibacterial, anti-tubercular, anti-HIV or alpha-lycosidase inhibition (Dai et al. 2015). Moreover, triazoles are widely used as pesticides for control of fungi which cause crop diseases (Cano and Santiago 2014). Application of the chemical protection in the form of fungicides has improved the modern agriculture by the increase of quality and yields of produced crops (Lucas et al. 2015).

Commercial triazole fungicides are represented by a diverse group of compounds applied for vegetable and fruit protection or material preservation (e.g., wood) (Han et al. 2014; Stamatis et al. 2015). Tebuconazole belongs to the triazole group of biocides and is used for the control of mildew, rust, net blotch, root rot, and seed-borne diseases. The most commonly available formulations are emulsifiable concentrates and wettable powders due to

the low solubility in water (Šiviková et al. 2013; Zhang et al. 2015). Tebuconazole exhibits moderate toxicity to freshwater fish and a half-life in soil equal to 49–610 days under aerobic conditions (Bernabò et al. 2016; Muñoz-Leoz et al. 2011). The main action mode is the inhibition of the 14 α -demethylase in ergosterol biosynthesis, an important component in fungal cell membranes, by influencing the cytochrome P450 enzyme activity (Ngo et al. 2016; Bordagaray et al. 2013). Recently, ILs which are based on 1,2,3- and 1,2,4-triazolium heterocycles have found interest as materials for energy-rich applications such as explosives and propellant fuels, solvents, catalysts, efficient CO₂ absorbents or antibacterial and chiral compounds (Brauer et al. 2015; Nagarajan and Kandasamy 2014; Reeder et al. 2016; Singh and Gardas 2016). Additionally, it is possible to synthesize protic and aprotic triazolium ILs with fungicidal properties (Pernak et al. 2015; Zabielska-Matejuk et al. 2015) or polymeric ILs (Zhang and Yuan 2016). The main purpose of this work was to prepare novel DILs exhibiting strong herbicidal and fungicidal properties. Studies were conducted due to the fact that currently there is a small amount of information on DILs based on tebuconazole and herbicidal acids in the literature. The synthesis of new dicationic liquids is important because it allows to obtain one compound indicating more than one biological activity that can be used as a versatile preparation with comprehensive efficacy.

Experimental

Materials

1,4-Dibromobutane (99%, CAS 110-52-1), 1,6-dibromohexane (96%, CAS 629-03-8), 1,8-dibromooctane (98%, CAS 4549-32-0), 1,10-dibromodecane (97%, CAS 4101-68-2), 1,12-dibromododecane (98%, CAS 3344-70-5) were obtained from Sigma-Aldrich and used without further purification. Tebuconazole (98%, CAS 107534-96-3) was purchased from Pestinova. Other chemicals and all solvents were obtained from Avantor Performance Materials Poland S.A. and used as received.

General

NMR spectra (¹H and ¹³C) were prepared in deuterated dimethylsulfoxide containing TMS as the internal standard. Measurements were carried out using Varian Mercury 300 or Varian VNMR-S 400 MHz spectrometers. Elemental analyses were performed at the Adam Mickiewicz University, Poznan (Poland).

Thermal analysis

Thermogravimetric analysis was performed using a Mettler Toledo Stare TGA/DSC1 unit. Samples between 2 and 10 mg were placed in aluminium pans and heated from 30 to 450 °C at a heating rate of 10 °C min⁻¹ under the flow of nitrogen.

Thermal transition temperatures of the prepared salts were determined using a Mettler Toledo Stare DSC1 apparatus under nitrogen. Samples between 5 and 15 mg were placed in aluminum pans and heated from 25 to 120 °C at a heating rate of 10 °C min⁻¹ and cooled with an intracooler at a cooling rate of 10 °C min⁻¹ to – 100 °C and then heated again to 120 °C.

Synthesis of triazolium dibromides

A mixture of appropriate dibromoalkane (0.05 mol) and 50 mL of acetonitrile was placed in a semi-automated system EasyMax 102 (Mettler Toledo) equipped with a 100 mL glass reactor, magnetic stirring bar and reflux condenser. Next, tebuconazole (0.1 mol) was added and the reaction was carried at 80 °C for 72 h. After that time, the homogeneous mixture was cooled to 25 °C and acetonitrile was removed by rotary evaporator (Büchi). Next, the obtained dibromides salts were purified by washing three times with hot hexane (50 mL) and dried under reduced pressure at 60 °C for 24 h.

Synthesis of DILs

Appropriate triazolium dibromide (0.01 mol) was dissolved with 20 mL of methanol in 50 mL glass reaction EasyMax 102 (Mettler Toledo) equipped with magnetic stirring bar. Next, potassium hydroxide (0.02 mol) in the form of a methanolic solution (10 mL) was added and the mixture was stirred for 1 h at 25 °C. After the anion exchange reaction, the solution was cooled to 0 °C and potassium bromide was filtered off. Afterwards, an appropriate herbicidal acid (MCPA, Dicamba, 0.02 mol) was introduced into the obtained methanolic solution of triazolium dihydroxides. The neutralization reaction was conducted for 1 h at 25 °C. Then, the synthesized DILs were purified by addition of anhydrous acetone (20 mL) and the residual precipitate was filtered. Finally, the solvent was evaporated and products were dried under reduced pressure at 60 °C for 24 h.

Tetramethylene-1,4-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[(4-chloro-2-methylphenoxy)acetate] (1a)

¹H NMR (DMSO-*d*₆, 300 MHz) δ (ppm) = 0.96 (s, 18H), 1.57–1.81 (m, 4H), 1.88 (br. s, 4H), 2.13 (s, 6H), 2.20 (m,

2H), 2.58–2.67 (m, 2H), 4.21 (s, 4H), 4.39 (br. s, 4H), 4.54 (br. s, 4H), 6.69 (d, *J* = 8.7 Hz, 2H), 7.05 (dd, *J* = 8.7, 2.7 Hz, 2H), 7.11 (d, *J* = 2.7 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 4H), 9.49 (s, 2H), 10.85 (s, 2H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ (ppm) = 16.0, 25.4, 25.5, 25.6, 29.7, 36.6, 38.1, 46.4, 56.2, 68.2, 74.8, 112.8, 122.7, 125.9, 127.9, 128.2, 129.4, 130.0, 130.2, 141.6, 144.0, 144.6, 156.1, 170.8; calcd (%) for C₅₄H₆₈Cl₄N₆O₈ (*M* = 1070.97): C 60.56, H 6.40, N 7.85; found: C 60.31, H 6.62, N 7.56.

Hexamethylene-1,6-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[(4-chloro-2-methylphenoxy)acetate] (2a)

¹H NMR (DMSO-*d*₆, 300 MHz) δ (ppm) = 0.96 (s, 18H), 1.24 (br. s, 4H), 1.57–1.80 (m, 8H), 2.13 (m, 8H), 2.56–2.66 (m, 2H), 4.25–4.31 (m, 8H), 4.55 (m, 4H), 6.69 (d, *J* = 8.7 Hz, 2H), 7.05 (dd, *J* = 8.7, 2.7 Hz, 2H), 7.12 (d, *J* = 2.7 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 4H), 9.48 (s, 2H), 10.86 (s, 2H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ (ppm) = 16.0, 24.4, 25.5 (3C), 28.5, 29.6, 36.5, 38.1, 47.2, 56.3, 68.1, 74.7, 112.8, 122.8, 125.9, 127.9, 128.2, 129.5, 130.0, 130.3, 141.6, 144.0, 144.5, 156.0, 170.8; calcd (%) for C₅₆H₇₂Cl₄N₆O₈ (*M* = 1099.03): C 61.20, H 6.60, N 7.65; found: C 61.49, H 6.33, N 7.88.

Octamethylene-1,8-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[(4-chloro-2-methylphenoxy)acetate] (3a)

¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm) = 0.96 (s, 18H), 1.17 (br. s, 8H), 1.57–1.80 (m, 8H), 2.01–2.08 (m, 2H), 2.13 (s, 6H), 2.56–2.63 (m, 2H), 4.19 (s, 4H), 4.27 (m, 4H), 4.52–4.61 (m, 4H), 6.68 (d, *J* = 8.8 Hz, 2H), 7.03 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.11 (d, *J* = 2.6 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 4H), 7.28 (d, *J* = 8.2 Hz, 4H), 9.46 (s, 2H), 10.91 (s, 2H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm) = 16.0, 25.2, 25.5, 27.9, 28.8, 29.6, 36.4, 38.1, 47.3, 56.4, 68.3, 74.7, 112.8, 122.5, 125.8, 127.8, 128.1, 129.4, 130.0, 130.2, 141.6, 144.0, 144.5, 156.1, 170.6; calcd (%) for C₅₈H₇₆Cl₄N₆O₈ (*M* = 1127.08): C 61.81, H 6.80, N 7.46; found: C 61.57, H 7.03, N 7.25.

Decamethylene-1,10-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[(4-chloro-2-methylphenoxy)acetate] (4a)

¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm) = 0.97 (s, 18H), 1.12–1.17 (m, 12H), 1.59–1.67 (m, 8H), 2.02–2.10 (m, 2H), 2.14 (s, 6H), 2.56–2.63 (m, 2H), 4.27 (m, 8H), 4.56 (m, 4H), 6.70 (d, *J* = 8.8 Hz, 2H), 7.05 (dd, *J* = 8.7, 2.7 Hz, 2H), 7.13 (d, *J* = 2.6 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.4 Hz, 4H), 9.42 (s, 2H), 10.79 (s, 2H); ¹³C

NMR (DMSO- d_6 , 100 MHz) δ (ppm) = 16.0, 25.4 (2C), 25.5 (2C), 28.3, 28.7, 29.0, 29.6, 36.5, 38.1, 47.4, 56.4, 67.7, 74.7, 112.8, 122.8, 125.9, 127.9, 128.1, 129.5, 130.0, 130.2, 141.6, 143.9, 144.4, 155.9, 170.6; calcd (%) for $C_{60}H_{80}Cl_4N_6O_8$ ($M=1155.13$): C 62.39, H 6.98, N 7.28; found: C 62.12, H 6.77, N 7.43.

Dodecamethylene-1,12-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[4-chloro-2-methylphenoxy]acetate] (5a)

1H NMR (DMSO- d_6 , 400 MHz) δ (ppm) = 0.97 (s, 18H), 1.12–1.18 (m, 16H), 1.61–1.82 (m, 8H), 1.98–2.07 (m, 2H), 2.15 (s, 6H), 2.56–2.64 (m, 2H), 4.22 (s, 4H), 4.30 (m, 4H), 4.52–4.63 (m, 4H), 6.70 (d, $J=8.8$ Hz, 2H), 7.03 (dd, $J=8.7, 2.6$ Hz, 2H), 7.11 (d, $J=2.6$ Hz, 2H), 7.15 (d, $J=8.4$ Hz, 4H), 7.27 (d, $J=8.4$ Hz, 4H), 9.49 (s, 2H), 10.95 (s, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ (ppm) = 16.0, 25.4, 25.5 (2C), 28.4, 28.9, 29.0, 29.6, 36.4, 38.1, 47.4, 56.5, 68.2, 74.7, 112.8, 122.8, 125.8, 127.8, 128.1, 129.4, 130.0, 130.2, 141.6, 144.0, 144.5, 156.1, 170.8; calcd (%) for $C_{62}H_{84}Cl_4N_6O_8$ ($M=1183.19$): C 62.94, H 7.16, N 7.10; found: C 63.16, H 6.95, N 7.30.

Tetramethylene-1,4-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[3,6-dichloro-2-methoxybenzoate] (1b)

1H NMR (DMSO- d_6 , 300 MHz) δ (ppm) = 0.97 (s, 18H), 1.55–1.81 (m, 4H), 1.95 (br. s, 4H), 2.18–2.28 (m, 2H), 2.59–2.69 (m, 2H), 3.78 (s, 6H), 4.46 (br. s, 4H), 4.55 (br. s, 4H), 7.04 (d, $J=8.6$ Hz, 2H), 7.16–7.20 (m, 6H), 7.28 (d, $J=8.4$ Hz, 4H), 9.50 (s, 2H), 10.70 (s, 2H); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ (ppm) = 25.4, 25.5, 25.6, 29.7, 36.6, 38.0, 46.5, 56.1, 61.0, 74.8, 125.1, 125.2, 126.7, 127.5, 128.1, 130.0, 130.2, 140.7, 141.6, 144.1, 144.4, 151.1, 165.9; calcd (%) for $C_{52}H_{62}Cl_6N_6O_8$ ($M=1111.80$): C 56.18, H 5.62, N 7.56; found: C 56.31, H 5.89, N 7.77.

Hexamethylene-1,6-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[3,6-dichloro-2-methoxybenzoate] (2b)

1H NMR (DMSO- d_6 , 300 MHz) δ (ppm) = 0.98 (s, 18H), 1.28 (br. s, 4H), 1.58–1.85 (m, 8H), 1.95 (br. s, 4H), 2.12–2.22 (m, 2H), 2.59–2.69 (m, 2H), 3.79 (s, 6H), 4.33 (m, 4H), 4.59 (br. s, 4H), 7.05 (d, $J=8.7$ Hz, 2H), 7.16–7.20 (m, 6H), 7.28 (d, $J=8.4$ Hz, 4H), 9.50 (s, 2H), 10.72 (s, 2H); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ (ppm) = 24.5, 25.5 (2C), 28.6, 29.7, 36.5, 38.1, 47.2, 56.2, 61.0, 74.8, 125.1, 125.2, 126.8, 127.4, 128.1, 130.0, 130.2, 140.5, 141.6, 144.1, 144.3, 151.1, 166.0; calcd (%) for $C_{54}H_{66}Cl_6N_6O_8$ ($M=1139.86$): C 56.90, H 5.84, N 7.37; found: C 57.14, H 6.07, N 7.56.

Octamethylene-1,8-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[3,6-dichloro-2-methoxybenzoate] (3c)

1H NMR (DMSO- d_6 , 400 MHz) δ (ppm) = 0.99 (s, 18H), 1.19 (br. s, 8H), 1.61–1.68 (m, 2H), 1.74–1.82 (m, 6H), 2.10–2.18 (m, 2H), 2.60–2.67 (m, 2H), 3.80 (s, 6H), 4.32 (m, 4H), 4.61 (br. s, 4H), 7.05 (d, $J=8.5$ Hz, 2H), 7.16–7.20 (m, 6H), 7.29 (d, $J=8.5$ Hz, 4H), 9.48 (s, 2H), 10.71 (s, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ (ppm) = 25.3, 25.5 (3C), 28.0, 28.9, 29.6, 36.5, 38.1, 47.4, 56.4, 61.0, 74.8, 125.1, 125.3, 126.7, 127.5, 128.1, 130.0, 130.2, 140.6, 141.6, 144.1, 144.3, 151.1, 165.9; calcd (%) for $C_{56}H_{70}Cl_6N_6O_8$ ($M=1167.91$): C 57.59, H 6.04, N 7.20; found: C 57.31, H 6.30, N 7.44.

Decamethylene-1,10-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[3,6-dichloro-2-methoxybenzoate] (4b)

1H NMR (DMSO- d_6 , 400 MHz) δ (ppm) = 0.99 (s, 18H), 1.13–1.19 (m, 12H), 1.60–1.68 (m, 2H), 1.74–1.84 (m, 6H), 2.10–2.18 (m, 2H), 2.59–2.67 (m, 2H), 3.79 (s, 6H), 4.32 (m, 4H), 4.61 (br. s, 4H), 7.09 (d, $J=8.6$ Hz, 2H), 7.18 (d, $J=8.5$ Hz, 2H), 7.24 (d, $J=8.6$ Hz, 4H), 7.29 (d, $J=8.6$ Hz, 4H), 9.44 (s, 2H), 10.62 (s, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ (ppm) = 25.4, 25.5, 28.3, 28.7, 29.0, 29.6, 36.5, 38.1, 47.5, 56.3, 61.0, 74.8, 125.2, 125.3, 127.4, 127.5, 128.1, 130.0, 130.2, 139.2, 141.5, 144.0, 144.2, 151.3, 165.9; calcd (%) for $C_{58}H_{74}Cl_6N_6O_8$ ($M=1195.96$): C 58.25, H 6.24, N 7.03; found: C 58.01, H 6.41, N 7.26.

Dodecamethylene-1,12-bis[1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol] di[3,6-dichloro-2-methoxybenzoate] (5b)

1H NMR (DMSO- d_6 , 400 MHz) δ (ppm) = 0.99 (s, 18H), 1.13–1.20 (m, 16H), 1.61–1.69 (m, 2H), 1.74–1.85 (m, 6H), 2.07–2.13 (m, 2H), 2.59–2.66 (m, 2H), 3.80 (s, 6H), 4.33 (m, 4H), 4.61 (m, 4H), 7.05 (d, $J=8.4$ Hz, 2H), 7.16–7.20 (m, 6H), 7.28 (d, $J=8.4$ Hz, 4H), 9.48 (s, 2H), 10.74 (s, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ (ppm) = 25.4, 25.5 (2C), 28.4, 28.8, 28.9, 29.0, 29.6, 36.5, 38.1, 47.5, 56.4, 61.0, 74.8, 125.1, 125.2, 126.7, 127.5, 128.1, 130.0, 130.2, 140.5, 141.6, 144.0, 144.3, 151.2, 165.9; calcd (%) for $C_{60}H_{78}Cl_6N_6O_8$ ($M=1224.02$): C 58.88, H 6.42, N 6.87; found: C 58.59, H 6.13, N 7.08.

Antifungal activity

Six species of fungi obtained from the Institute of Plant Protection-NRI collection were used: *Sclerotinia sclerotiorum*, *Botrytis cinerea*, *Fusarium culmorum*, *Fusarium*

oxysporum, *Colletotrichum* sp., and *Monographella nivalis*. The sample of tested DILs was dissolved in 4 mL of methanol, then added to a sterile medium cooled to 50 °C (PDA—potato dextrose agar, Difco™). The concentration of the studied salt in the medium was 10, 100 or 1000 ppm. Liquid medium containing the tested salts was distributed on the Petri dishes (diameter of 50 mm). The 4 mm disks of the examined fungi were placed in the center of the Petri dish. In the control sample, the fungi were grown on PDA with the addition of sterile solvent. The tested salts were compared with the commercial fungicide Tebu 250 EW containing tebuconazole as an active substance. The plates were incubated at room temperature until the mycelium in the control reached the edge of the Petri dish. Afterwards, the diameter of the mycelium was measured, subtracting the initial diameter of the disk with the fungus (4 mm). Three replications were performed for each experimental sample. The results were subjected to Student–Newman–Keuls’s analysis to test for significant differences between control and samples with addition of DILs. Fungicidal activity was calculated on the basis of the following equation:

$$\% \text{ activity} = \left(\frac{A - B}{A} \right) \cdot 100\%, \quad (1)$$

where A is diameter of the mycelium without addition of tested substances and B is diameter of the mycelium with addition of tested substances.

Herbicidal activity

The activity of the prepared DILs was tested on common lambsquarters and oilseed rape. Seeds were sown into pots (0.5 L) and kept in a greenhouse at the temperature of 20 °C, humidity of 60% and photoperiod 16/8 h (day/night). The plants were treated by the herbicide at 6 leaves growth stage (BBCH 16). A spray solution was prepared by dissolving the synthesized salts in a mixture of water and ethanol (1:1 v/v) at the amount corresponding to the dose 400 g of MCPA or 200 g dicamba per 1 ha. Commercial herbicides: Chwastox Extra 300 SL (300 g of sodium and potassium salts of MCPA in 1 L) and Dikamba 480 SL (480 g Dicamba in 1 L) were chosen as references. All the treatments were applied using a moving sprayer (APORO, Poznan, Poland) with TeeJet 110/02 at-fan nozzles (TeeJet Technologies, Wheaton, IL, USA) delivering 200 L of spray solution per 1 ha at 0.2 MPa pressure. The distance from the nozzles to the tips of the plant was equal to approx. 40 cm. The study was carried out in four replications in a randomized setup. After application, the plants were placed again in a greenhouse under the above-mentioned environmental conditions. A weed control was evaluated visually 2 weeks after the treatment using a scale of 0 (no effect) to 100% (complete weed destruction).

Results and discussion

A three-step method for the synthesis of new DILs is shown in Scheme 1. Preparation of precursors in the form of triazolium dibromides (**1–5**) was the first part of the synthesis.

Scheme 1 Preparation of dibromide salts (**1–5**) and dicationic ILs (**1a–5d**)

Table 1 Prepared triazolium dibromides

Bromide	<i>n</i>	Yield (%)	<i>T_m</i> (°C)
1	4	93	218–220
2	6	87	155–156
3	8	94	236–237
4	10	98	140–142
5	12	90	180–181

Table 2 Synthesized triazole-based DILs

ILs	<i>n</i>	A	Yield (%)
1a	4	MCPA	93
2a	6	MCPA	97
3a	8	MCPA	94
4a	10	MCPA	95
5a	12	MCPA	92
1b	4	Dicamba	98
2b	6	Dicamba	95
3b	8	Dicamba	97
4b	10	Dicamba	94
5b	12	Dicamba	95

The quaternization of the nitrogen atom in the N-4 position using acetonitrile as a solvent was carried out according to the modified method described by Jin et. al (2006). The quaternization agents were dibromoalkanes with an alkyl chain length of 4–12 carbon atoms. In addition, tebuconazole possessing a 1,2,4-triazole group functionalized in the N-1 position was used as the triazole compound in the quaternization reaction. The results of the precursor synthesis are shown in Table 1.

All the obtained triazolium dibromides were in the form of white solids with a high melting point (*T_m*). The highest values were measured for the bromides with the linker containing 4 and 8 methylene groups and were approximately at 217 and 235 °C, respectively. For the remaining bromides, *T_m* was below 200 °C and ranged from 140 to 180 °C. Lowest value was measured for bromide 4. The efficiency of the first stage was equal to or exceeded 87%.

After purification and drying, the obtained triazolium bromides were used as a substrate in the second step of the synthesis, in the exchange of bromide anions to hydroxides according to the methodology described earlier for herbicidal DILs (Niu et al. 2018; Niemczak et al. 2015). The obtained methanolic solutions of the precursor in the form of hydroxides were used in the last stage of the method, in the neutralization reaction using two selected herbicidal acids: 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 3,6-dichloro-2-methoxybenzoic acid (Dicamba). The applied method of synthesis was characterized by a high yield ranging from 91 to 98% (Table 2).

Triazolium DILs with the Dicamba anion were amorphous, noncrystalline solids and compounds (**1–5a**) based on the MCPA were in the form of waxes.

All synthesized DILs exhibited low solubility in water. On the other hand, the obtained compounds displayed excellent solubility in polar solvents such as methanol or DMSO. In addition, solubility was not observed in hexane and toluene.

The chemical structures of the obtained ILs were confirmed by analysis of ¹H and ¹³C NMR spectra. In the case of a linker chain, protons of the methyl group adjacent to the N-4 nitrogen occurred at approx. 4.30 ppm. The remaining signals of the linker were present at 1.82, and its extension caused the appearance of additional peaks of methylene groups in the form of wide singlets at approx. 1.26 (ILs **2a**, **2b**), 1.17 (ILs **3a**, **3b**) and two peaks in the range of 1.11–1.21 in the case of other DILs. The signals of protons in the form of a doublet derived from the aromatic ring appeared in all spectra at 7.17 and 7.28 ppm. In addition, the presence of the *tert*-butyl group was confirmed by the signals at approx. 0.96 ppm. The protons of the methylene group located on the N-1 nitrogen of the triazole group were present in all spectra in the range 4.48–4.62 ppm. Furthermore, the remaining protons of methylene groups adjacent to the aromatic ring and *tert*-butyl group occurred in the form of separated signals at approx. 2.16 and 2.62, and also in the range of 1.57–1.82, overlapping with the signal derived from the linker chain. The changes in the chemical shift of the H-3 and H-5 proton signals are presented in Table S7. The quaternization reaction resulted in a strong shift of the two singlets derived from the protons of the triazole group in comparison to the pure tebuconazole (7.95 and 8.19 ppm, spectrum in CDCl₃) due to the redistribution of electron density (Golubyatnikova et al. 2012). For the obtained DILs, the proton H-3 was determined in the range 9.42–9.50 ppm, and the signal from the proton H-5 appeared in the range 10.62–10.95 ppm. The highest values of proton chemical shifts occurred for DILs **1–5a** in the case of an anion derived from MCPA acid. In addition, the extension of the linker resulted in slight changes in the chemical shift values, however, regardless of the type of anion, the lowest value in the group was caused by the linker with ten carbon atoms.

Properties of synthesized ILs (glass transition and decomposition temperatures) are shown in Table 3. The *T_{onset}* values for triazolium DILs were observed in the range from 201 to 223 °C. Generally, it was found that the trend of the anions on the stability can be described as follows: MCPA > Dicamba. A similar relationship also occurred for the previously described dicationic HILs (Niemczak et al. 2015). In the case of monocationic HILs, the effect of type of an anion on stability may vary depending on the used cation. However, most of the ILs with Dicamba anion were less stable compared to compounds based on other

Table 3 Thermal properties of prepared DILs

ILs	T_g^a (°C)	T_{onset5}^b (°C)	$T_{onset50}^c$ (°C)	Steps of degradation
1a	20	223	314	2
2a	19	209	298	3
3a	15	218	303	2
4a	18	213	322	3
5a	10	212	298	3
1b	46	219	281	2
2b	35	203	266	2
3b	38	201	263	2
4b	30	207	306	2
5b	32	201	267	3

^a T_g —glass transition temperature^b T_{onset5} —decomposition temperature of 5% sample^c $T_{onset50}$ —decomposition temperature of 50% sample

herbicidal acids (Pernak et al. 2016). Analyzing the thermal stability of the obtained DILs with different length of the linker chain, no significant differences were observed between the compounds in the homologue series. The lack of a strong influence of the linker on the thermal stability also occurred for other DILs (Shirota et al. 2011). Analyzes if the decomposition temperatures at which 50% of weight lost occurred ($T_{onset50}$) showed that all the ILs were characterized by thermal stability from 263 to 314 °C and the effect of the anion is the same as in the case T_{onset5} . The obtained DILs mostly exhibit two or three thermal decomposition steps. In addition, elongation of linker influenced the decomposition behavior and can cause a more complex degradation. Additionally, exothermal effects were observed for all DILs decomposition. The highest values (163 J g⁻¹) were measured for IL **1a**.

The phase transition of synthesized DILs was evaluated by differential scanning calorimetry (DSC) and only glass transition temperatures (T_g) were observed in all cases. A previously reported study showed that the length of the alkyl linkage chain has a weak influence on the T_g values (Pitawala et al. 2009). In our work, T_g values of triazolium DILs significantly decrease with the extension of the linker. The lowest values in a given series of compounds occurred in the case of DILs with the length of the chain between cations equal to 12 atoms of carbon. Moreover, the influence of the anion on the T_g is higher than length of linker and the trend of the anions is: Dicamba > MCPA. ILs with the MCPA anion was characterized by the lowest values (T_g = 9.9–19.5).

In contrast to antibacterial studies (Al-Mohammed et al. 2015), there are currently no reports regarding activity of DILs against fungi causing plant diseases. Fungicidal activities of DILs obtained in our work and their precursors

(triazolium dibromides) were determined for six species of fungi: *Sclerotinia sclerotiorum*, *Botrytis cinerea*, *Fusarium culmorum*, *Fusarium oxysporum*, *Colletotrichum*, and *Monographella nivalis*. The mentioned fungi are pathogens which infect a wide range of plants, including economically important crops and are responsible for heavy agricultural losses every year. The ascomycete fungus *S. sclerotiorum* may infect more than 400 plant species, including canola, dry bean, sunflowers or lettuce, causing difficult to control diseases commonly known as white mold or Sclerotinia head rot. Yield losses may reach even 50–70%, depending on the season and region (Di et al. 2016; Dunker and von Tiedemann 2004; Koch et al. 2007). *B. cinerea*, also known as the gray mold, is a necrotrophic pathogen which infects a wide range of fruit, vegetable and ornamental crops. Due to notable losses in agriculture, this fungus has been considered as the second most dangerous phytopathogen worldwide (Li et al. 2016; Dean et al. 2012). *Fusarium* genus comprises many species which are able to colonize different plants and are one of the most economically important fungi. *F. culmorum* is the common pathogen of many important plants causing seedling blight, foot rot, and head blight (Wagacha and Muthomi 2007; Batur-Ciesniewska and Suchorzynska 2011). Similarly, *F. oxysporum* represents a worldwide widespread species responsible for Fusarium wilt, Fusarium crown and root (McGovern 2015). In addition to diseases caused by *Fusarium* genus, the serious problem is associated with the production of mycotoxins, including trichothecenes, fumonisins, and zearalenone. Additionally, *Colletotrichum* sp. and *M. nivalis* are common pathogens responsible for anthracnose diseases (Taga et al. 2015) and snow mold (Zeun et al. 2013), respectively. In case of results obtained at a concentration of 10 ppm (Fig. 1), the highest activity against *S. sclerotiorum* fungi was observed for DILs containing Dicamba anions and in most cases the efficacy was higher than 90% or comparable to the reference formulation. Commercial formulation Tebu 250 EW showed activity equal to 91.7 ± 8.9%. Notably lower results were measured for DILs with bromide and MCPA anions, for which the highest activity was 65.2 ± 6.6 (**3**) and 38.4 ± 2.3 (**4a**), respectively. *B. cinerea* fungus proved to be more resistant to the triazolium DILs. In the best cases (**4**, **5a**), the activity reached approx. 80%. In contrast to the tests carried out using *S. sclerotiorum*, the compounds containing the Dicamba anion were less effective. Their activity did not exceed 60%. Analysis of the results of fungicide activity against *F. culmorum* at the lowest concentration of compounds (Fig. 2) showed that the best efficacy was observed in case of compounds with a bromide anion (88.4 ± 2.3). For the other DILs, only salts derived from MCPA exceeded 80% activity. In the case of studies performed on *Colletotrichum* sp. (Fig. 3), similar to the results obtained for *F. oxysporum*, the type of anion had little effect on the ability of compounds

Fig. 1 Fungicidal activity of DILs against *Sclerotinia sclerotiorum* and *Botrytis cinerea*

to inhibit fungal growth. The highest results were equal to approx. 70% at the lowest concentration and activities were much lower compared to the reference compound. The dose of active substance in the amount of 10 ppm was too low in the case of studies carried out using *M. nivalis*. Five of the tested compounds (**2**, **5**, **1a**, **1b**, **5b**) showed very low activity (less than 20%) against this fungus. In addition, a pool result of 43.1 ± 0.6 was also obtained for the reference formulation. Similar activity was measured for compounds with bromide anions (**3**, **4**), MCPA (**3a**) and Dicamba (**3b**). However, only for Tebu 250 EW there was an increase of inhibition of fungal growth to 100% as a result of increasing the concentration to 100 ppm. In case of the other compounds, the best result was equal to $92.0 \pm 1.3\%$ for **4b**. Only an increase of the dose of DILs to 1000 ppm allowed to achieve 100% efficacy.

Fig. 2 Fungicidal activity of DILs against *Fusarium culmorum* and *Fusarium oxysporum*

Commercial fungicide Tebu 250 EW was used as the reference (ref).

In the previous article (Niemczak et al. 2015), our studies have concentrated on determination the herbicidal activity of DILs with long alkyl chains ($C_{10}H_{21}$) in the cation. Nevertheless, the results described by Cao et al. (Niu et al. 2018) have shown that the activity of a herbicidal acid such as 2,4-D could be improved by preparation of its dicationic ILs forms without long substituents. In this work, a similar dependence has been demonstrated, namely that DILs with short alkyl substituents exhibited high efficacy, similar to monocation herbicidal ionic liquids. DILs **1a** and **1b** showed the best results (Table 4). In the case of common lambsquarters, higher efficiencies by 20% compared to commercial products have been demonstrated by these ILs. In the case of oilseed rape, the difference was smaller and amounted to 10%. All the tested DILs have shown better activity than

Fig. 3 Fungicidal activity of DILs against *Colletotrichum* sp. and *Monographella nivalis*

Table 4 The herbicidal activity of DILs against common lambsquarters and oilseed rape

Treatment	Efficacy (%)	
	Lambsquarters	Oilseed rape
1a	87	55
2a	85	55
3a	65	45
4a	60	50
5a	68	45
MCPA reference	65	45
1b	85	38
2b	82	35
3b	80	35
4b	60	30
5b	58	10
Dicamba reference	58	20

reference herbicides. The herbicidal effect may be improved by the presence of the triazole group in the cation, because triazole inhibits the growth of certain plant species (Yang et al. 2014).

Conclusions

In summary, it can be established that dicationic triazolium salts show a variety of activities against fungi and plants. Their effectiveness, in the case of fungi, depends primarily on the concentration, but also on the type of anion and the length of the linker. In studies using concentrations between of 100 and 1000 ppm of active substance, most compounds showed efficacy close to the reference substance (tebuconazole). Additionally, the fungicidal activity of the compounds increased with the lengthening of the linker. Mostly, the highest efficiency occurred for the salts containing linker with 8 and 10 carbon atoms. In addition to the fungicidal activity, the obtained compounds can be applied as herbicides, due to their high biological activity, as demonstrated by tests carried out using common lambsquarters and oil-seed rape. However, the influence of linker length on herbicidal properties is much less notable in comparison to antifungal activity. Regardless of the type of anion, the compounds with the longest linker exhibited the lowest herbicidal efficacy.

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