### ABSTRACT
The goal of this research was to obtain and characterize ionic liquids based on a bisammonium cation and both 4-chloro-2-methylphenoxyacetate (MCPA) and l-tryptophanate anions. The concept of including two structurally different anions was utilized to achieve improved biological activity, while crucial functional traits could be designed by modifying the cation. The synthesis process was efficient and resulted in high yields. Subsequent analyses (nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy, and high-performance liquid chromatography (HPLC)) confirmed the chemical structure, purity, and molar ratio of ions in the obtained compounds. The described compounds are novel and have not been previously described in the literature. Evaluations of physicochemical properties indicated that the obtained double-salt ionic liquids (DSILs) exhibited high thermal stability, high solubility in water, and surface activity. A biological activity assessment using greenhouse tests revealed that the herbicidal efficiency of the studied DSILs was notably increased compared to the reference commercial herbicide (even by ~50% in the case of oilseed rape), which could be attributed to their high wettability toward hydrophobic surfaces. The compounds also efficiently inhibited the growth of several microbial species, with minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC)/minimum fungicidal concentration (MFC) values at the level of several μg·mL⁻¹. The length of the spacer and alkyl substituent in the cation notably influenced the physicochemical and biological properties of the DSILs, which allowed us to design the structures of the obtained compounds in accordance with needs. The presented results confirm the high application potential of the described DSILs and provide a new and promising path for obtaining new and efficient plant-protection agents.

### 1. INTRODUCTION
Auxins are phytohormones that control many aspects of plant growth and development. Auxins play a leading role in the mechanisms of cell division, growth, development, and aging of fruit, shoots, and roots. Indole acetic acid (IAA) is the main natural auxin. IAA can be produced by organisms via Trp-dependent and Trp-independent mechanisms. Trp-dependent IAA biosynthesis pathways use tryptophan as a precursor, which is converted into indolylpyruvate (IPA) by TAA transaminase and then into IAA by flavin monoxygenase.

Synthetic auxins, which were designed and obtained based on the structures and functions of natural auxins, are widely used in agrochemistry. They are used in agriculture not only as growth stimulants but also as herbicides. Weeds are a major problem in crop plant production, as they can reduce crop yields by 34%. Therefore, research regarding new herbicides is needed and has been one of the most common research topics in the Weed Science Society of America (WSSA) in recent years. The WSSA distinguishes 35 classes of herbicides, and WSSA Group 4 comprises agents that behave like natural auxins. They mimic the action of IAA by binding to receptors. Examples of synthetic auxins with herbicidal activity include 1-naphthylacetic acid (1-NAA), 2,3,6-trichlorobenzoic acid (TBA), 2,4-dichloro-phenoxyacetic acid (2,4-D), 4-chloro-2-methylphenoxy acetic acid (MCPA), 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB), and 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB). Their direct impacts on yields and the signaling pathways and resistance mechanisms in weeds are under investigation.
Table 1. Yields of the Synthesized DSILs and the Results of DSC/TG Analysis

| DSILs | −(CH$_2$)$_n$− | R       | yield [%] | molar ratio of anions MCPA:TRP | $T_\text{g}$ [°C] | $T_\text{c}$ [°C] | $T_{5\%}$ [°C] | $T_{50\%}$ [°C] |
|-------|----------------|---------|-----------|-------------------------------|-----------------|----------------|----------------|----------------|
| 1     | (CH$_2$)$_{12}$− | C$_{16}$H$_{33}$ | 97        | 1:0.94                        | 18              | 139            | 241            |                 |
| 2     | (CH$_2$)$_{12}$− | C$_{14}$H$_{29}$ | 97        | 1:0.93                        | 24              | 147            | 258            |                 |
| 3     | (CH$_2$)$_{12}$− | C$_{12}$H$_{25}$ | 96        | 1:0.97                        | 23              | 159            | 272            |                 |
| 4     | (CH$_2$)$_{12}$− | C$_{10}$H$_{21}$ | 99        | 1:1.01                        | 11              | 162            | 288            |                 |
| 5     | (CH$_2$)$_{12}$− | C$_{8}$H$_{17}$  | 97        | 1:0.91                        | 17              | 33             | 79             | 160            |
| 6     | (CH$_2$)$_{12}$− | C$_{6}$H$_{13}$  | 99        | 1:0.95                        | 8               | 136            | 250            |                 |
| 7     | (CH$_2$)$_{12}$− | C$_{4}$H$_{9}$   | 95        | 1:0.97                        | 15              | 132            | 266            |                 |
| 8     | (CH$_2$)$_{12}$− | C$_{2}$H$_{5}$   | 98        | 1:1.05                        | 21              | 129            | 279            |                 |
| 9     | (CH$_2$)$_{12}$− | C$_{10}$H$_{21}$ | 98        | 1:0.93                        | 11              | 142            | 299            |                 |
| 10    | (CH$_2$)$_{12}$− | C$_{8}$H$_{17}$  | 98        | 1:0.95                        | 14              | 147            | 315            |                 |
| 11    | (CH$_2$)$_{12}$− | C$_{6}$H$_{13}$  | 96        | 1:1.05                        | 11              | 136            | 276            |                 |
| 12    | (CH$_2$)$_{12}$− | C$_{4}$H$_{9}$   | 96        | 1:0.93                        | 3               | 134            | 284            |                 |
| 13    | (CH$_2$)$_{12}$− | C$_{2}$H$_{5}$   | 96        | 1:0.93                        | 2               | 135            | 293            |                 |
| 14    | (CH$_2$)$_{12}$− | C$_{10}$H$_{21}$ | 95        | 1:0.93                        | 15              | 142            | 325            |                 |
| 15    | (CH$_2$)$_{12}$− | C$_{8}$H$_{17}$  | 95        | 1:0.96                        | 10              | 131            | 328            |                 |
| 12a   | (CH$_2$)$_{12}$− | C$_{10}$H$_{21}$ | 97        | 2:0                           | −27             | 213            | 271            |                 |
| 12b   | (CH$_2$)$_{12}$− | C$_{8}$H$_{17}$  | 98        | 0.2                           | 16              | 152            | 315            |                 |
| 12c   | (CH$_2$)$_{12}$− | C$_{6}$H$_{13}$  | 96        | 0.2 (IAA)                     | −14             | 213            | 282            |                 |
| 12d   | (CH$_2$)$_{12}$− | C$_{4}$H$_{9}$   | 97        | 0.2 (IBA)                     | −21             | 238            | 296            |                 |

$^\text{a}$ $T_m$, melting point; $T_c$, temperature of crystallization; $T_\text{g}$, glass-transition temperature; $T_{5\%}$, decomposition temperature of 5% of the sample; $T_{50\%}$, decomposition temperature of 50% of the sample.

Invention of 2,4-D in 1945, 41 types of weeds have developed resistance to this herbicide.$^{10,11}$

Ionic liquids (ILs) are compounds that consist only of ions, and their melting point does not exceed 100 °C. Originally, they were produced to replace volatile solvents. In addition, they are used in the synthesis, catalysis, and electrochemical and chemical analysis of bioactive compounds. They can serve, inter alia, as antistatic or dispersing agents as well as adjuvants. Due to the multitude of cation–anion combinations, it is possible to design compounds with virtually any characteristics. The conversion of biologically active compounds into ILs expands the spectrum of their applications. Examples include herbicides, fungicides, feeding deterrents, and growth regulators. ILs containing anions with a regulatory effect have also been described in the literature. The conversion of 2-chloroethytrimethylammonium chloride into an IL results in a compound with retained bioactivity that exhibits unique properties depending on the anion included.$^{12}$ Ammonium salts containing the IBA anion and an amino acid cation show regulatory properties toward germination and shoot and root development.$^{13}$ A convenient method of obtaining ammonium salts with an l-tryptophanate anion, which shows plant growth regulation activity and improved physicochemical properties, was described in previous reports.$^{14}$

Herbicidal ionic liquids (HILs) are a new approach to known bioactive compounds. The latest reviews outline the broad scope of this research topic, which provides numerous opportunities that still lie ahead of researchers in this field.$^{15}$ HILs that incorporate many herbicidal anions have been investigated, including MCPA,$^{22}$ 2,4-D,$^{23}$ dicamba,$^{24}$ 2,4-DP,$^{25}$ nicosulfuron,$^{26}$ and a nonselective pelargonate of natural origin.$^{27}$ Fungicidal ionic liquids are mainly based on compounds containing a triazole group.$^{28}$ Examples of such cations include tebuconazole and propiconazole derivatives.$^{29}$ It is possible to convert fungicidal diols, e.g., dibenzothiophene-5,5-dione, into ILs by replacing the hydroxyl groups with quaternary ammonium groups. Thus, the obtained dichloride retains its fungicidal character.$^{30}$ The combination of two fungicidal cations, thiamethazole and imazalil, with a single anion allows improved properties to be achieved due to the synergistic effect of bioactive ions complemented by the physicochemical properties of the anion.$^{31}$ Quaternary ammonium salts that combine herbicidal and fungicidal properties are also known.$^{32}$ Such compounds can combine the tebuconazole or propiconazole cation with an herbicidal anion, which results in the formation of ILs with dual properties.$^{33}$ Chemical modification consisting of joining two tebuconazole molecules with an alkyl spacer allows bisammonium cations to be obtained, and their combination with herbicidal anions results in compounds with both herbicidal and fungicidal properties.$^{34}$ Bifunctional HILs are an example of compounds in which biological activity is derived from both the anion and the cation. The transformation of MCPA and 2-chloroethytrimethylammonium chloride into an IL results in a product that exhibits both an anion-derived herbicidal effect and cation-derived growth regulator activity.$^{35}$ The combination of herbicidal dicamba with tropine characterized by regulatory properties has also been reported.$^{36}$ Double-salt herbicidal ionic liquids (DSHILs) are a particular example of ILs with activity derived from more than one ion. In their case, the ammonium cation is converted into an ionic liquid with two anions in a fixed proportion. DSHILs designed in this way are characterized by herbicidal activity derived from both anions and by physicochemical properties provided by the cation.$^{37,38}$ The most advanced strategy for the synthesis of DSHILs is the combination of two anions with biological activity with a bisammonium cation containing two quaternary nitrogen atoms. Such compounds may include one anion with herbicidal properties and another of natural origin, which leads to unique physicochemical and herbicidal properties.$^{39}$ HILs are characterized by improved properties compared to commercially available products containing the same active substances. Through the use of a rationally designed cation, it is possible to obtain a compound with improved physicochemical properties that translate into herbicidal activity.$^{40}$
Considering the above-mentioned information, it seems reasonable to assume that attention should be focused on the combination of natural and synthetic auxins and the possibility of converting them into DSILs. The aim of this study was to develop sophisticated methods for the synthesis of efficient and environmentally friendly DSILs containing bisammonium cations and both MCPA and L-tryptophanate anions. In addition, the herbicidal and antimicrobial activities of the obtained DSILs were evaluated. To complete the analysis of the results, the influence of anions combination in DSILs on the tested physicochemical and biological properties was also investigated.

2. RESULTS AND DISCUSSION

2.1. Synthesis. The DSILs presented in Table 1 were synthesized by a two-step process. In the first step of the synthesis, the bromide anions of the bisammonium dibromide were exchanged for hydroxide anions using a highly alkaline ion-exchange resin in anhydrous methanol, according to the method previously described by our research team. The second step used an Easy-Max reactor to perform a direct acid-base reaction between the bisammonium hydroxides, MCPA and L-tryptophan anions. In addition, the herbicidal and antimicrobial activities of the obtained DSILs were evaluated. To complete the analysis of the results, the influence of anions combination in DSILs on the tested physicochemical and biological properties was also investigated.

![Scheme 1. Synthesis of DSILs 1-15 and 12a-12d](image)

Synthesis of DSILs 1-15

\[ \text{OH} \quad \left(\text{CH}_2\right)_n \quad \text{N} \quad \text{OH} \quad \text{OH} + \text{HA}^1 + \text{HA}^2 \rightarrow \text{A}^1 \quad \text{N} \quad \text{N} \quad \text{A}^2 + 2\text{H}_2\text{O} \]

\[ \text{A}^1 = \]

\[ \text{A}^2 = \]

Synthesis of DSILs 12a-12d

\[ \text{OH} \quad \left(\text{CH}_2\right)_{12} \quad \text{N} \quad \text{OH} \quad \text{OH} + 2\text{HA} \rightarrow \text{A} \quad \text{N} \quad \left(\text{CH}_2\right)_{12} \quad \text{N} \quad \text{A} + 2\text{H}_2\text{O} \]

\[ \text{A} = \]

\[ \text{R}^1 = \text{CHNH}_2\text{COO}^-, \text{COO}^-; \text{CHCH}_2\text{COO}^- \]

The results of elemental analysis (CHN) are included in the Supporting Information (Table S1) and confirmed the high purity of the obtained DSILs. The compounds were not previously described in the literature.

The structures of the synthesized DSILs were confirmed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy analyses, and the results are included in the Supporting Information (Table S1 and Figures S1-S57). In the \(^1\)H NMR spectra of the DSILs (1-15, 12a-12d), chemical shifts originating from the cation and both anions were observed. Characteristic signals associated with the TRP anion occurred at \(\sim3.65\) ppm (from the \(\text{CH}^-\text{NH}_2\) proton) and \(7.18\) ppm from the \(\text{CH}\) group in the pyrrole ring. Characteristic resonance signals of the MCPA anion occurred at \(\sigma [\text{ppm}] = 2.25\) ppm (from the \(\text{CH}_3\) group of the aromatic ring) and \(4.40\) ppm (from the \(\text{CH}_2\text{COO}^-\) group). For the IAA anions, characteristic resonance signals distinguishing them from the TRP anions occurred at \(\sim3.59\) ppm (from the \(\text{CH}_2\) group), and for...
the IBA anions—at 2.35, 2.02, and 2.80 ppm (respectively, from the CH₂—CH₂—CH₃ groups). In turn, the resonance signals at ~1.70 to 0.90 ppm confirm the presence of carbon chains in the bisammonium cation. In the ¹³C NMR spectrum, there were two signals characteristic of carboxyl groups, located at ~180 ppm for the TRP anion and at ~176 ppm for the MCPA anion. A resonance signal at ~16 ppm confirms the presence of a methyl group attached to the aromatic ring in the MCPA anion. For the IAA anions, the characteristic chemical shifts distinguishing them from the TRP anions occurred at σ [ppm] = 30.65 ppm (from the CH₂ group), and those distinguishing them from the IBA anions occurred at ~27.35, 27.15, and 30.55 ppm (respectively from the CH₂—CH₂—CH₃ groups). The presence of the bisammonium cation was confirmed by resonance signals in the range of 31–14 ppm. In the FT-IR spectra, the characteristic signals from the TRP anion appeared at the following approximate V_max values [cm⁻¹]: 650 (benzene ring), 745 (CH, rocking vibration), 880 (substituted ring 1,4 distribution), 997 (C=N, stretching vibration), 1097 (aryl group), 1140 (C=C, stretching vibration), 1230 (CH₂ wagging vibration), 1400 (<C=O, stretching vibration), 1460 (−COO⁺, stretching vibration), and 1560 (C=O, stretching vibration). The presence of the MCPA anion was confirmed by signals with the following V_max [cm⁻¹] values: 721 (Cl—C, stretching vibration), 800 (substituted ring 1,2 distribution), 900 (substituted ring 1,1 distribution), 1240 (═C=O—C, stretching vibration), and 1500 (−COO⁺, stretching vibration). After analyzing the FT-IR spectra of DSILs 12a–12d, all signals characteristic of TRP, MCPA, IAA, and IBA anions were observed. Comparing the spectra of compounds 12b and 12c with that of 12d, the differences in the spectra were small—the signal from the C=N group at 997 cm⁻¹ disappeared, and an additional signal appeared at a V_max of 721 cm⁻¹ (−CH₂=, rocking vibration). Characteristic signals of bisammonium cations were recorded in the range of 2850–3000 cm⁻¹, originating from the CH₂ff groups. ILs containing TRP and MCPA anions (1–15) were subjected to quantitative high-performance liquid chromatography (HPLC) analysis. The application of ion pair chromatography allowed the separation and quantification of both anions. The retention times were equal to 6.2 and 11.7 min for TRP and MCPA anions, respectively. An exemplary chromatogram is presented in Figure 1. The operating conditions are included in the Supporting Information (Figure S58).

The measured retention times matched the retention times of the standards. Based on the calibration curves, the molar ratio of the anions was calculated (Table 1). HPLC chromatograms are included in the Supporting Information (Figures S58–S74). Both anions were confirmed to be present in equimolar amounts. In the case of monoanionic ILs, the concentrations of MCPA and TRP were confirmed for 12a and 12b, respectively. The observed variations did not exceed the measurement error. NMR spectroscopy, FT-IR and HPLC analyses fully confirmed the structures of the synthesized DSILs.

2.2. Thermal Analysis. In the literature regarding a series of bis-cationic compounds, the influence of the cation core (imidazolium, ammonium, or phosphonium) and spacer length on the thermal properties has been widely described.⁴⁴⁻⁴⁶ Described systems containing two identical cations were mainly influenced by the incorporation of two different cation cores into one compound, which resulted in the formation of liquid crystals.⁴⁵⁻⁴⁷ Most bis-cationic compounds described in the literature include a single popular type of anion, e.g., major halides such as bromide, chloride, or NTf₂ and BF₄ in the case of ILs. On the other hand, the effect of the incorporation of two different anions and one cation was described in a monocationic system containing fractional anions at a molar ratio of glyphosate/MCPA equal to 8.48:0.152, and the thermal behavior of the product underwent only slight changes.⁴⁸ Similarly, in studies regarding the combination of the ammonium cation and the MCPA–Dikamba anionic system, no significant changes in thermal properties were observed.⁵⁷ However, the results of our research examining equimolar amounts of TRP-MCPA anions showed more drastic changes in the thermal properties of the resulting ILs. For all prepared DSILs (Table 1), only a glass transition occurred, which suggests that the incorporation of the examined anion system reduced the molecular order to a minimum. Most likely, the most ordered system occurs in the same cation with two bromide anions, which was previously

Figure 1. HPLC chromatogram of DSIL 1.
described in the literature. For example, in the case of bis(N-dodecyl-N,N-dimethylammonium) dibromides described in the literature with spacers ranging from 2 to 10 carbon atoms, thermal phase transitions, such crystallization and melting points, were observed in all cases. These dibromides also showed correlations between the length of the spacer and the number and type of mesophases (ordered smectic phases and/or smectic liquid crystals). In our study, no similar observation could be established.

For DSILs 1–15, the tendency of a glass transition with the elongation of alkyl substituents was not uniform. In the case of DSILs with a hexyl spacer (1–5), the glass-transition temperature ($T_g$) was generally unchanged, ranging from 17 to 24 °C. Only for DSIL 4 did the glass-transition temperature decrease to 11 °C. A similar tendency was observed for DSILs 6–10, with slightly lower glass-transition temperatures equal to 8, 15, and 14 °C for DSILs 6, 7, and 10, respectively. In the case of the dodecyl alkyl substituent (8), an increase in $T_g$ reaching 21 °C was observed. For DSILs 11–15 with longer spacers, the glass-transition temperatures were lower for decyl (13) and dodecyl (14) groups, reaching 3 and 2 °C, respectively. In the case of extreme substituent lengths in DSILs 11 and 15, the glass-transition temperature was higher and reached ~10 °C. Only in the case of compound 5, additional crystallization at 33 °C and a melting point at 79 °C were observed. The occurrence of a glass transition indicates an amorphous character of the obtained ILs. Detailed analysis (HPLC) showed that the molar ratios of the anions (MCPA/TRP) ranged from 1:0.93 to 1:1.03 (Table 1). The detailed influence of molar ratios of the anions in the range of 2:0 to 0:2 was studied.

The influence of l-tryptophan anion molar ration in DSIL 2 is presented in Figure 2. The curve is “s-shaped”. This characteristic is commonly achieved in polymeric systems with various reactive additives. The occurrence of hydrogen bond donors (e.g., NH or NH$_2$) acceptors (e.g., carbonyl or ether group), and aromatic rings in both MCPA and TRP anions in the obtained ILs as well as the character of the curve (Figure 2) indicated complex intramolecular interactions. The TAGA results indicated that the studied DSILs were thermally stable up to 131 °C. The compound containing only the MCPA anion (12a) decomposed at 213 °C, and the DSIL containing the same cation and two anions of TRP (12b) decomposed at 152 °C. For DSILs containing a mixed MCPA/TRP anion system with six carbon atoms in the spacer (1–5), decomposition occurred from 139 to 160 °C. Elongation of the spacer to eight carbon atoms (6–10) resulted in a minimal reduction in thermal stability from 129 (8) to 147 °C (10). Further spacer elongation (11–15) did not produce significant differences in terms of thermal stability, with decomposition occurring at 131 °C for 15 and 142 °C for 14. The exchange of one MCPA anion for TRP caused a decrease in the thermal stability of the IL. The elongation of the alkyl substituent lowered the dynamics of thermal decomposition for DSILs (11–15), and the value of $T_{50\%}$ increased from 276 to 328 °C with increasing alkyl chain lengths.

### 2.3. Chemical Stability.

The chemical stability of aqueous solutions of the obtained DSIL 12 was tested at 80 °C. In the framework of this study, $^1$H and $^{13}$C NMR spectra were obtained before and after heating. In the $^1$H NMR spectrum of DSIL 12 after heating, a decrease in signal integration and intensity by 20–80% and shifts in resonance signals in the $^1$H spectra by ~1.5 ppm were observed. Analysis of the $^{13}$C NMR spectra of DSIL 12 after heating indicated the disappearance of the signals from carbon atoms in the indolyl ring ($\sigma$ [ppm] = 138.68, 129.43, 125.30, 120.80, 120.10, and 112.39) and the carbon atom in the carbonyl group ($\sigma$ = 180.94 ppm). The observed differences clearly indicate a change in the chemical structure of DSIL 12 after heating. The conversion of l-tryptophan to an ion reduced its chemical stability, which was also observed in our previous research regarding amino acid ILs with tetraalkylammonium cations. A comparison of the NMR spectra of DSIL 12 and its degradation products is shown in Figures S75 and S76.

### 2.4. Solubility Studies.
The solubility test was carried out using popular organic solvents in ascending order of polarity index values according to Snyder’s scale. The results of the test are presented in Table 2.

The tested DSILs 1–15 were insoluble in low-polar and apolar solvents such as ethyl acetate, toluene, or hexane. The exception was chloroform, in which all salts were soluble despite its low polarity and aprotic nature, which may have been related to its donor ability to form hydrogen bonds with the tested salts. The obtained DSILs 1–15 were soluble in polar solvents. The exception was dimethyl sulfoxide (DMSO), in which the solubility decreased with the elongation of the R substituent in the bisammonium cation. Comparison of the obtained results with our previous studies indicated that the elongation of the l-tryptophan anion increased the solubility of all DSILs in the tested solvents. The solubility of l-tryptophan and MCPA in water is limited, at 11 and 725 mg L$^{-1}$, respectively. The conversion and combination of l-tryptophan and MCPA into ionic forms resulted in an over 100-fold improvement of their solubility in water. In the case of DSILs containing the same two anions (12a–12d), a decrease in water solubility was observed compared to the analogue of DSIL 12, which was caused by the higher molar fraction of the anion that was almost insoluble in water.

### 2.5. Surface Activity.

Surface activity was determined for aqueous solutions of DSILs 1–15 in the concentration range of 5 $\times$ 10$^{-2}$ to 2 $\times$ 10$^{-6}$ mol L$^{-1}$ at 25 °C. The following surface activity parameters were evaluated: the critical micelle concentration (CMC), surface tension at CMC (γCMC), efficiency of surface adsorption at an air–water interface (pC$_{20}$), and contact angle (CA). The results are included in the Supporting Information (Tables S2–S4 and Figure S77). The determined surface tension at the CMC point ranged between 33 and 43 mN m$^{-1}$. The lowest CMCs occurred for DSILs 3, 8, and 13 with dodecyl substituents. For all DSILs, the CMC parameter increased with elongation from the hexyl to octyl spacers and then decreased (Figure 3A). After analyzing the influence of the alkyl substituents, it was noted
that the CMC parameter decreased with elongation from the octyl to dodecyl substituents and then increased from the dodecyl to hexadecyl substituents (Figure 3B). The CMC value ranged from 18 to 0.9 mmol L\(^{-1}\). The relationship between the CA value and the length of the alkyl group is presented in Figure 3C. The value of CA increased linearly with the elongation of the alkyl substituent in the bisammonium cation, which resulted from higher hydrophobic interactions between the longer chains.\(^{51,52}\) The elongation of the alkyl substituent resulted in an increase in the contact angle from 50 to 81° for the alkyl substituent.

### 2.6. Herbicidal Activity

The herbicidal activity of the obtained DSILs was determined on the basis of biological tests performed in a greenhouse using common lambsquarters (*Chenopodium album* L.) and winter oilseed rape (*Brassica napus* L.) as test plants. The test results for DSILs 2, 4, 5, 7, 9, 10, 12, 14, and 15 are presented in Figure 4. The greenhouse test confirmed that most of the synthesized DSILs showed higher herbicidal effectiveness than the commercial herbicide containing MCPA in the form of potassium and sodium salts.

### 2.7. Antimicrobial Activity

Microbial contamination is a common phenomenon that is harmful to animal and human health; hence, the antimicrobial properties of the studied DSILs were tested. The biological activity of DSILs 1−15 was evaluated using Gram-positive and Gram-negative bacteria as well as yeasts. The obtained results are presented in Figure 6A−C, along with the analysis of the influence of the pC\(_{20}\) parameter on the antimicrobial activity. The test was repeated after 4 weeks to determine the effect of chemical stability on the antimicrobial activity. The calculated mean values of the minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC), and minimum fungicidal concentration (MFC) are included in the Supporting Information (Tables S5−S8). All studied DSILs showed biological activity against all test microorganisms. The strongest inhibitory effects against the growth of the tested microorganisms were observed for DSILs 3, 8, 12, and 12a−12d, the biological activity of which was higher than or comparable to that of the didecyldimethylammonium chloride [DDA][Cl] and benzalkonium chloride [BA][Cl] used for comparative purposes. The DSILs exhibited strong antimicrobial effects toward Gram-positive and Gram-negative bacteria as well as yeasts. The antimicrobial activity of the tested DSILs remained at a comparable level after a month of storage, and a slight decrease in biological activity was observed only in a few cases. The literature states that the biological activity of DSILs...
increases with the elongation of the alkyl substituents, which was also observed in our study for compounds 1−15.36,55 After analyzing the influence of the chemical structure of the bisammonium cation, it was noted that the antimicrobial activity increased with the elongation of the R substituent—the values of the MIC, MBC, and MFC parameters decreased. For the DSILs (5, 10, and 15) with the longest R substituents in the bisammonium cation (R = 16), an increase in antimicrobial activity was not observed. This phenomenon was described in the related literature as a "cut-off", which applies to ILs and cationic surfactants.56,57 Comparing the results obtained for DSILs 12 and 12a−12d, it was noted that the use of two anions with the same chemical structure increased the activity only against Pseudomonas aeruginosa and Serratia marcescens. For the remaining microorganisms, the antimicrobial and antifungal activities did not change, which may have been related to the progressive degradation of anions. The role of the bisammonium cation was thus dominant.56 The antimicrobial activity of the applied DSILs was greatly influenced by the surface activity, e.g., the parameter pC20.56 For the obtained DSILs, the highest antimicrobial efficacy was recorded in the optimal pC20 range. In the case of DSILs that exhibited lower or higher pC20 values than the optimum, lower antibacterial and antifungal efficacy was observed. In addition, a parabolic relationship was observed between the MIC or MFC and pC20, which has also been reported in the literature.56,57 After comparing the impact of the tested DSILs on the growth of

![Figure 3. Impact of number of carbon atoms in the spacer on CMC (A) and the number of carbon atoms in the alkyl substituent on CMC (B) and CA (C) in DSILs 1−15 at 25 °C.](https://doi.org/10.1021/acsomega.1c05048)
individual groups of microorganisms, it can be concluded that Gram-positive bacteria and yeasts showed greater sensitivity to applied compounds than Gram-negative bacteria. *Moraxella catarrhalis* showed the highest sensitivity among Gram-negative bacteria, while *Micrococcus luteus* was the most sensitive among Gram-positive bacteria.

3. CONCLUSIONS

This study presents the synthesis and characterization of a homologous series of novel DSILs, which comprise a single cation and two different anions. The concept of combining bisammonium cations with different alkyl substituents with L-tryptophanate and MCPA as anions allowed us to obtain a group of compounds with a set of properties that perfectly fit the requirements of modern agrochemicals. A series of analyses, including NMR, FT-IR, and HPLC, confirmed that the employed synthesis method is feasible for obtaining the target structures with high yields (95−99%) and equimolar ratios of anions. Subsequent studies (i.e., elemental analysis, assessments of halide and water contents, and DSC/TG) allowed us to determine that the DSILs were characterized by high purity and thermal stability. It was observed that the length of the spacer and alkyl substituent in the cation notably influenced the studied physicochemical properties (thermal behavior, solubility in different solvents, and surface activity), which allowed us to design the structures of the obtained compounds in accordance with needs. The high water solubility resulting from the conversion of L-tryptophan and MCPA to anionic forms is of particular importance from the practical perspective of preparing spray solutions. The subsequent evaluation of biological activity indicated that all of the studied DSILs exhibited high herbicidal activity, which, in most cases, exceeded that of the reference commercial herbicide agent (even by ~50%). Their high efficiency in eliminating weeds corresponds well with their high wettability of hydrophobic surfaces, i.e., high affinity to interact with plant leaves. Each of the studied compounds also exhibited excellent antimicrobial activity, which was comparable to or higher than that of didecyl(dimethylammonium) chloride and benzalkonium chloride. The low MIC and MBC/MFC values may be attributed to the high surface activity of the cationic component and can be considered another merit, as the compounds may protect crops from pathogenic microorganisms. It should be noted that L-tryptophan as an anion is characterized by lower stability; hence, the compounds should be stored under appropriate conditions. However, its degradation occurs slowly and does not affect the functional properties in a significant manner. The presented results confirm the high application potential of the described DSILs and provide a new and promising path for obtaining new and efficient plant-protection agents.

4. MATERIALS AND METHODS

4.1. Materials. The following chemicals were purchased from Sigma-Aldrich (Poznan, Poland): 1,6-dibromohexane (purity 96%), 1,8-dibromooctane (purity 98%), 1,12-dibromododecane (purity 98%), dimethyloctylamine (purity 97%), decyldimethylamine (purity 90%), dimethyldodecylamine (purity 97%), dimethyltetradecylamine (purity 95%), hexadecyl(dimethyl)amine (purity 95%), L-tryptophan (purity 98%), and Dowex-Monosphere 550A anion exchange resin. (4-Chloro-2-methylphenoxy)acetic acid [MCPA] (purity 97%) was obtained from CIECH Sarzyna (Nowa Sarzyna, Poland). All solvents (methanol, acetonitrile, acetone, hexane, toluene, chloroform, isopropanol, DMSO, and ethyl acetate) were from Avantor (Gliwice, Poland). Deionized water with conductivity <0.1 μS·cm⁻¹, from demineralizer HLP Smart 1000 (Hydrolab, Poland), was used for solubility and surface activity measure-
ment. All reagents and solvents were used without further purification. As a reference, Chwastox Extra 300 SL (300 g MCPA per 1 L, CIECH Sarzyna, Poland) was used as a commercial herbicide. Microbiological media used for the studies were purchased in BioMaxima (Poland).

4.2. Synthesis. The appropriate bisammonium dibromide (0.05 mol) obtained in our earlier studies was dissolved with 50 mL of anhydrous methanol in a 100 mL reaction glass equipped with a mechanical stirrer. The anionic resin Dowex-Monsphere 550A (40 mL) in the form of a methanolic suspension was added, and the mixture was stirred for 8 h at 25 °C. After the anion exchange reaction, the resin was filtered and rinsed three times using small amounts of methanol. Then, a stoichiometric amount of L-tryptophan and MCPA was added to the bisammonium hydroxide solution. All of the neutralization reactions were conducted at 25 °C in a Mettler Toledo semiautomated system reactor equipped with a glass electrode. The solvent was evaporated under vacuum in a

Figure 6. Influence of pC20 on MBC against Gram-positive bacteria (A), Gram-negative bacteria (B), and MFC against yeasts (C).
Table 3. Conditions for the Cultivation of Microorganisms

| microorganism          | medium                              | temperature [°C] |
|------------------------|-------------------------------------|------------------|
| S. aureus ATCC 33862   | nutrient agar                       | 37               |
| S. epidermidis ATCC 12228 | brain heart infusion agar         | 37               |
| E. faecalis ATCC 19433 | brain heart infusion agar           | 37               |
| B. subtilis ATCC 11774 | nutrient agar                       | 37               |
| M. luteus ATCC 4698    | trypsinase soy agar                 | 30               |
| E. coli ATCC 8739      | nutrient agar                       | 37               |
| P. aeruginosa ATCC 9027 | nutrient agar                     | 37               |
| S. marcescens ATCC 8100 | tryptase soy agar               | 30               |
| P. vulgaris ATCC 49132 | brain heart infusion agar           | 37               |
| M. catarrhalis ATCC 25238 | tryptase soy agar            | 30               |
| C. albicans ATCC 10231 | Sabouraud agar with chloramphenicol | 37               |
| R. rubra               | Sabouraud agar with chloramphenicol | 30               |

rotary evaporator, and the product was dried under reduced pressure (5 mbar) at 40 °C for 48 h. The synthesized DSILs were stored in UV-blocking vacuum desiccators over P4O10 at 20 °C.

4.3. Analysis. The 1H and 13C NMR studies were performed using a Varian XL300 spectrophotometer. Deuterated methanol was used as the solvent, and tetramethylsilane was the reference. The elemental analyses (CHN) were performed using an Elementar Analyser Vario EL III at the Adam Mickiewicz University, Poznan (Poland).

FT-IR spectra were recorded using a semiautomated EasyMax 102 system connected with a ReactIR 15 spectrometer with a probe and MCT detector and a 9.5 mm AgX probe with a diamond tip (Mettler Toledo system). The data were collected from 640 to 3000 cm⁻¹ with high resolution.

HPLC analyses were conducted using a Dionex UltiMate 3000 unit equipped with a UV-DAD detector operating at 280 nm wavelength. Thermo Scientific Hypersil Gold C18 150 mm/4.6mm with a stationary particle size of 5 μm was used as the column. The mobile phase was a gradient mixture of 0.1 M ammonium formate, 10% v/v formic acid, and acetonitrile in ratios of 99:1:0 at 0 min, 25:1:74 at 15 min, and 99:1:0 at 20 min under a 1 mL min⁻¹ flow rate. Time of analysis was 20 min, and injection volume was equal to 20 μL. Concentrations were determined on the basis of calibration curve in the range of 10–500 ppm. The water content was determined using an Aquastar volumetric Karl–Fischer titration with Composite S solution as the titrant and anhydrous methanol as a solvent.

4.4. Thermal Analysis. The TGA/DSC1 Mettler Toledo apparatus was used. The thermal analysis apparatus was calibrated by measuring the following standards: In (purity 99.999%, Tm = 156.49 °C, ΔH = 29.38 J g⁻¹), Pb (purity 99.999%, Tm = 327 °C, ΔH = 22.25 J g⁻¹), Zn (purity 99.998%, Tm = 418.78 °C, ΔH = 106.53 J g⁻¹), Al (purity 99.999%, Tm = 660.03 °C, ΔH = 340.15 J g⁻¹). Thermogravimetric measurements were performed at 10 °C min⁻¹ from room temperature to 500 °C under dynamic nitrogen atmosphere (50 mL min⁻¹), using about 4–5 mg of sample in aluminum pans. Thermal transition temperatures were determined by DSC, with a Mettler Toledo Star DSC1, under dynamic nitrogen atmosphere (50 mL min⁻¹), using about 4–5 mg of sample in aluminum pans. Measurements were performed in the range −100 up to 105 °C.

4.5. Chemical Stability. To evaluate the chemical stability of a selected DSIL, 0.1 g was dissolved in 50 mL of water and heated at 80 °C for 2 days. The solvent was then evaporated using a rotary evaporator. The obtained compound was dried using a vacuum dryer at 60 °C for 24 h. Changes in the structure of the compound were determined on the basis of NMR spectroscopy analysis.

4.6. Solubility. Water and nine popular organic solvents characterized by varying polarity were selected for the solubility test and arranged in order of decreasing Snyder’s polarity index: water, 9.0; methanol, 6.6; DMSO, 6.5; acetonitrile, 6.2; acetone, 5.1; isopropanol, 4.3; ethyl acetate, 4.3; chloroform, 4.1; toluene, 2.3; and hexane, 0.0. The solubility of the obtained salts in organic solvents was determined according to the methodology previously described in Vogel’s Textbook of Practical Organic Chemistry. The sample of DSILs (0.1000 ± 0.0001 g) was introduced into a specific volume of solvent. The analyses were performed at 25 °C. Depending on the volume of solvent used, three outcomes have been recorded: “high solubility” applies to salts that dissolved in 1 cm³ of the solvent, “limited solubility” applies to compounds that dissolved in 3 cm³ of the solvent, and “low solubility” applies to DSILs that did not dissolve in 3 cm³ of the solvent.

4.7. Surface Activity. Surface tension and contact angle values of DSILs were determined by the use of a DSA 100 analyzer (KRUS GmbH, Germany, accuracy ± 0.01 mN m⁻¹) at 25 °C. The surface tension was carried out using the shape drop method. Basically, the principle of this method is to form an axisymmetric drop at the tip of a needle of a syringe. The image of the drop (3 mL) is taken from a CCD camera and digitized. The surface tension (γ in mN m⁻¹) is calculated by analyzing the profile of the drop according to the Laplace equation. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy ± 0.1°C).

4.8. Herbicidal Activity. The biological studies were performed in a greenhouse with controlled environmental conditions: a temperature of 20 (±2) °C, humidity of 60%,
and a photoperiod of 16/8 h day/night using common lambquarters (C. album L.) and winter oilseed rape (B. napus L.) as the test plants. The plants were grown in 0.5 L plastic pots containing commercial peat-based potting material (pH 6). After emergence, the plants were thinned to five in each pot. Treatments were applied at the 4–6 leaf growth stage. The commercial product Chwastox Extra 300 SL (300 g of sodium and potassium salts of MCPA in 1 L) was used as a reference. DSILs were applied at a dose corresponding to 300 g of active ingredient (MCPA) per 1 ha. Commercial herbicide was used at the same doses of active ingredient. All tested DSILs and reference compounds were dissolved in water. The applications were conducted using a moving sprayer (APORO, Poznan, IL) delivering 200 L·ha⁻¹ of spray solution at an operating pressure of 0.2 MPa. The nozzle was moved above the plants at a 40 cm distance and at a constant speed of 3.1 m·s⁻¹. After treatment, the plants were again placed in a greenhouse under the environmental conditions mentioned above. The fresh weight of the plants was measured 2 weeks after treatment using a technical balance with an accuracy of 0.01 g (Sartorius BP 2000 S, Sartorius Göttingen, Germany). The study was carried out in four replications in a randomized setup. The error margin range represents standard errors of the mean (SEM). The SEM values were calculated according to the following equation

\[
SEM = s \cdot n^{-0.5}
\]

where SEM is the standard error of the mean, s is the sample standard deviation, and n is the number of replications.

4.9. Antimicrobial Activity. Antimicrobial tests were conducted using Gram-positive bacteria Staphylococcus aureus ATCC 33862, Staphylococcus epidermidis ATCC 12228, Enterococcus faecalis ATCC 19433, Bacillus subtilis ATCC 11774, and M. luteus ATCC 4698; Gram-negative bacteria Escherichia coli ATCC 8739, P. aeruginosa ATCC 9027, S. marcescens ATCC 8100, Proteus vulgaris ATCC 49132, and M. catarrhalis ATCC 25238; and yeasts Candida albicans ATCC 10231 and Rhodotorula rubra. Before the experiments, the microorganisms were propagated on appropriate agar media for 24 h. The experiments were performed on the day of complete drying of the obtained DSILs (29/09/2020) and after a 30-day period of storage of the samples under 5 °C refrigeration conditions (28/10/2020). The samples were stored refrigerated and protected from light. In each case, the ionic liquids were dissolved in water, resulting in a starting concentration of 2000 μg·mL⁻¹. The minimum inhibitory concentration (MIC) and the minimum bactericidal/fungicidal concentration (MBC/MFC) values were determined by the twofold dilution method in 96-microtiter plates. Twenty-four-hour cultures of microorganisms on slants were used to prepare a suspension in saline to achieve a 0.5 MacFarland density. Next, the solutions were diluted in Mueller–Hinton broth (for bacteria) or Sabouraud broth (for fungi) to obtain a density of 10⁶ CFU·mL⁻¹. A series of twofold dilutions of the tested ILs were prepared on microplates in the concentration range from 1000 to 0.5 μg·mL⁻¹. For this purpose, 100 μL of Mueller–Hinton or Sabouraud broth was introduced into the wells of sterile microplates, except for the first row, into which ionic liquid solutions with a concentration of 2000 μg·mL⁻¹ were introduced. Subsequently, 100 μL of the bacterial suspension was introduced into all wells, obtaining a final inoculum density of 5 × 10⁶ CFU·mL⁻¹. The negative control was the medium with the addition of ionic liquids, and the positive control was the culture of microorganisms without the addition of the inhibitory agent. The plates were incubated at the appropriate temperature for each microorganism (Table 3) for 24 h. The optical density of microbial growth was measured at a wavelength of 600 nm using a BioTek Epoch 2 microplate reader. The MIC value was defined as the concentration of the IL that inhibited the growth of the tested microorganism by at least 90%. The MBC/MFC value was determined by sport inoculation of 10 μL of microbial culture with the addition of ILs at a concentration equal to or higher than the determined MIC value (100% inhibition of bacterial growth based on spectrophotometric measurements).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05048.

1H NMR, 13C NMR, and FT-IR spectra of all compounds (Figures S1–S57), HPLC chromatograms for all compounds (Figures S58–S74), comparison of the NMR spectra of DSIL and its degradation products (Figures S75 and S76), surface tension isotherms for analyzed DSILs (Figure S77), elemental analysis of the compounds (Table S1), surface tension and contact angle of aqueous DSILs solutions (Tables S2–S4), and the calculated mean values of the MIC, MBC, and MFC (Tables S5–S8) (PDF)

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**Notes**

The authors declare no competing financial interest.
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