Synthesis of Novel Pyrazole Derivatives Containing Phenylpyridine Moieties with Herbicidal Activity

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Abstract: To discover new compounds with favorable herbicidal activity, a range of phenylpyridine moiety-containing pyrazole derivatives were designed, synthesized, and identified via NMR and HRMS. Their herbicidal activities against six species of weeds were evaluated in a greenhouse via both pre- and post-emergence treatments at 150 g a.i./hm². The bioassay revealed that a few compounds exhibited moderate herbicidal activities against Digitaria sanguinalis, Abutilon theophrasti, and Setaria viridis in post-emergence treatment. For instance, compounds 6a and 6c demonstrated 50% inhibition activity against Setaria viridis, which was slightly superior to pyroxasulfone. Thus, compounds 6a and 6c may serve as the new possible leading compounds for the discovery of post-emergence herbicides.

Keywords: synthesis; pyrazole; phenylpyridine; herbicidal activity

1. Introduction

Pyrazole-containing compounds, a class of five-membered heterocyclic compounds with simple synthetic routes, have been widely used in the study of biologically active molecules such as in medicine [1,2], pesticides [3,4], and veterinary drugs [5,6]. In the field of agriculture, a variety of small molecules containing pyrazole groups have been developed as pesticide products (Figure 1), such as fungicides [7,8], insecticides [9–12], and herbicides [13–15]. Zhang et al. demonstrated that a series of novel substituted pyrazole aminopropyl isothiocyanates exhibited certain herbicidal activity against Echinochloa crusgalli, Cyperus iria, Dactylis glomerata, and Trifolium repens [16]. A class of 1-acyl-3-phenylpyrazol benzophenones was prepared by Ye et al. using dimethylformamide dimethyl acetal and 1, 3-diphenylpropane-1, 3-dione as the starting materials, which showed good herbicidal activity [17]. Liu et al. reported that a class of novel pyrazole aromatic ketone derivatives exhibited excellent herbicidal activity against various broadleaf weeds treated post-emergence [18]. The promising pesticide pyroxasulfone [19] discovered by Kumiai Chemical is a pre-emergence herbicide that could provide excellent control of grass and broadleaf weeds in corn and soybean fields.
Substituted phenylpyridines discovered by Schaefer et al. exhibited good inhibition activity against weeds [20,21]. Substituted 3-(pyridin-2-yl)benzenesulfonamide derivatives disclosed by Liu et al. showed excellent inhibitory activity against a variety of weeds [22–24]. Du et al. also reported that a range of kresoxim-methyl derivatives containing phenylpyridine moieties exhibited higher inhibitory activities against broadleaf weeds than mesotrione [25,26].

Herein, 10 novel pyrazole derivatives containing phenylpyridine moieties were obtained via the principle of active substructure splicing, and the structures of these target compounds were confirmed by NMR and HRMS. In addition, the inhibitory activities of the resultant compounds against broadleaf and grass weeds were determined.

2. Results and Discussion

2.1. Chemistry

As can be seen from Schemes 1 and 2, all target compounds were obtained by multi-step reactions using substituted pyridines and ethyl 4,4,4-trifluoroacetacetate as starting materials. Intermediates A (4a–4e) were prepared from substituted pyridine and p-hydroxyphenylboronic acid via multi-step reactions, such as the Suzuki cross-coupling reaction, nucleophilic substitution reaction, Newman–Kwart rearrangement reaction, and hydrolysis reaction [27,28]. Intermediate B was obtained via a simple three-step reaction as per the previously disclosed method, using ethyl 4,4,4-trifluoroacetacetate as the starting material [29]. The target compounds 6a–6e were prepared via a nucleophilic substitution reaction from intermediates A and B; compounds 6a–6e were oxidized to yield compounds 7a–7e using 3-chloroperbenzoic acid as the oxidant, according to previously disclosed methods [30]. After synthesis, all target compounds were characterized via HRMS and NMR. The NMR and HRMS spectra of all the target compounds are shown in the Supplementary Materials.

2.2. Greenhouse Herbicidal Activity Assays

According to the herbicidal activity test results, none of the target compounds exhibited herbicidal activities for pre-emergence. As can be seen from Table 1, a few target compounds exhibited moderate herbicidal activities. Of these, at 150 g a.i./hm², compounds 6a and 6c exhibited 50–60% inhibitory activities when used for the post-emergence treatment of the weeds Digitaria sanguinalis (DS), Abutilon theophrasti (AT), and Eclipta prostrate (EP). Furthermore, the inhibitory activities of compounds 6a and 6c against EP were superior to pyroxasulfone.
From previous studies on the herbicidal activity of pyrazole derivatives, it can be seen that some reported pyrazole derivatives showed good herbicidal activity. According to the study of Zhou et al. [31], the herbicidal activity of some substituted phenylpyrazole derivatives against *Abutilon theophrasti*, at 150 g a.i./hm², was above 90%. Although

Table 1. The structures and herbicidal activities of pyrazole derivatives at a 150 g a.i./hm² post-emergence treatment dose in a greenhouse assay setting.

| Compound | Chemical Structure | Weed a |
|----------|--------------------|--------|
|          | R₁ | R₂ | EC | DS | SV | AT | AR | EP |
| 6a       | Cl | CF₃ | 0 b | 50 | 0  | 50 | 0  | 50 |
| 6b       | Br | Cl  | 0  | 0  | 0  | 30 | 0  | 30 |
| 6c       | Cl | F  | 0  | 60 | 0  | 60 | 0  | 50 |
| 6d       | F  | Cl  | 0  | 30 | 0  | 30 | 0  | 0  |
| 6e       | Cl | CH₃ | 0  | 0  | 0  | 20 | 0  | 0  |
| 7a       | Cl | CF₃ | 0  | 0  | 0  | 0  | 0  | 0  |
| 7b       | Br | Cl  | 0  | 0  | 0  | 0  | 0  | 0  |
| 7c       | Cl | F  | 0  | 0  | 0  | 20 | 0  | 0  |
| 7d       | F  | Cl  | 0  | 0  | 0  | 20 | 0  | 0  |
| 7e       | Cl | CH₃ | 0  | 0  | 0  | 0  | 0  | 0  |
| pyroxasulfone | / | | 60 | 75 | 60 | 50 | 50 | 0  |

a EC, *Echinochloa crus-galli*; DS, *Digitaria sanguinalis*; SV, *Setaria viridis*; AT, *Abutilon theophrasti*; AR, *Amaranthus retroflexus*; EP, *Eclipta prostrata*. b All the data were determined three times.
compounds 6a and 6c of this work exhibited moderate herbicidal activities, they could also be further optimized as lead compounds to obtain compounds with higher activity.

From Table 1, we can see that the herbicidal activities of compound 6 were obviously better than those of compound 7, indicating that the structure containing 4-(pyridin-2-yl)phenylene sulfide was beneficial to the improvement of the activity. According to the SAR of compound 6 in the field of herbicidal activity, when the 3-position of pyridine was a chlorine atom and the 5-position was a fluorine atom or a trifluoromethyl group, compound 6 exhibited the best herbicidal activity for post-emergence.

3. Materials and Methods

3.1. Instrumentation

All reagents and other materials were purchased from commercial sources and used without additional purification unless otherwise noted. A B-545 melting point instrument (Buchi, Hangzhou, China) was used to determine the melting point without calibration. A Bruker AV-400 spectrometer (Billerica, MA, USA) was used to generate NMR spectra with DMSO-<i>d</i><sub>6</sub> serving as the solvents. An Agilent 6545 Q-TOF LCMS spectrometer (Santa Clara, CA, USA) was used for mass spectrometry.

3.2. Synthesis

The synthesis approach for pyrazole derivatives containing substituted 4-(pyridin-2-yl)benzene moieties in this work is outlined in Scheme 1.

3.2.1. Synthesis of Intermediates A (4a–4e)

4-(3-Chloro-5-trifluoromethylpyridin-2-yl) thiophenol intermediate (4a) is taken as an example.

2,3-Dichloro-5-trifluoromethylpyridine (1.08 g, 5 mmol), potassium carbonate (1.38 g, 10 mmol), triphenylphosphorus (0.13 g, 10 mol%), p-hydroxybenzeneboronic acid (0.76 g, 5.5 mmol), palladium(II) acetate (5 mol%, 0.06 g), CH<sub>3</sub>OH (5 mL), and CH<sub>3</sub>CN (10 mL) were mixed and stirred at 50 °C for 6 h under N<sub>2</sub>. Thereafter, the mixture was extracted using ethyl acetate (30 mL × 3), rinsed using brine, and concentrated. The remaining residue was then recrystallized using ethanol and water as solvents at 70 °C to obtain 1.22 g of compound 1a.

Compound 1a (13.65 g, 50 mmol), 1,4-diazabicyclo[2.2.2]octane (11.22 g, 100 mmol), dimethylcarbamothioic chloride (11.22 g, 100 mmol), and N,N-dimethylformamide (250 mL) were mixed and stirred at 60 °C for 8 h. Thereafter, the mixture was extracted using ethyl acetate (100 mL × 3), rinsed using brine, and concentrated to give a yellow solid 2a, which was used in the next reaction without further purification.

The yellow solid 2a synthesized in the previous step and N-methyl pyrrolidone (100 mL) were stirred under reflux for 7 h under N<sub>2</sub>. Thereafter, the mixture was extracted using ethyl acetate (100 mL × 3), rinsed using brine, and concentrated to give a yellow solid 3a, which was used in the next reaction without further purification.

The yellow solid 3a (3.61 g, 10 mmol), 85% potassium hydroxide (0.69 g, 10.5 mmol), tetrahydrofuran (20 mL), and methanol (10 mL) were mixed and stirred at 20 °C for 10 h. Thereafter, the mixture was made more acidic using hydrochloric acid, extracted thrice using ethyl acetate (30 mL × 3), rinsed using brine, and concentrated. Residues were then purified via silica gel column chromatography using ethyl acetate (EA) and petroleum ether (PE) (<i>V</i><sub>EA</sub>:<i>V</i><sub>PE</sub>=1:10) to obtain 3.15 g of yellow solid of intermediate 4a.

3.2.2. Synthesis of Intermediate B

4-(Chloromethyl)-5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazole was prepared using the method disclosed previously, which is indicated in Scheme 2.

3.2.3. General Approach to the Synthesis of Compounds 6a–6e and 7a–7e

The target compounds 6a and 7a are taken as examples.
Compound 4a (0.44 g, 1.5 mmol), 60% NaH (0.12 g, 3 mmol), and N,N-dimethylformamide (10 mL) were mixed and stirred at 20 °C for 30 min under N2. Next, 4-(chloromethyl)-5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazole 5 (0.48 g, 1.8 mmol) was added followed by stirring for 4 h at 60 °C. Thereafter, the mixture was extracted thrice using ethyl acetate (30 mL × 3), rinsed using brine, and concentrated. Residues were then purified via silica gel column chromatography using ethyl acetate (EA) and petroleum ether (PE) (VEA:VPE = 1:10) to obtain 0.56 g of white solid of target compound 6a.

Compound 6a (0.20 g, 0.19 mmol) and 85% m-chloroperoxybenzoic acid (0.19 g, 0.93 mmol) in dichloromethane (5 mL) were mixed and stirred at 20 °C for 11 h. Thereafter, the mixture was evaporated to remove the solvent. Residues were then purified via silica gel column chromatography using ethyl acetate (EA) and petroleum ether (PE) (VEA:VPE=1:5) to obtain 0.07 g of white solid of target compound 7a.

3-chloro-2-(4-(((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)thio)phenyl)-5-methylpyridine (6b): White solid; Yield 72.1%; M.p. 68.3–70.4 °C. 1H NMR (400 MHz, DMSO-d6) δ: 8.73 (d, J = 2.1 Hz, 1H), 8.47 (d, J = 2.1 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.48 – 7.44 (m, 2H), 7.30 (t, J = 7.1 Hz, 1H), 4.15 (s, 2H), 3.79 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ: 157.96 (d, J = 5.9 Hz), 151.96 (d, J = 4.0 Hz), 143.69 (t, J = 3.7 Hz), 137.48 (q, J = 37.1 Hz), 136.96 (d, J = 5.4 Hz), 136.71, 135.58, 130.35, 129.59 (d, J = 4.6 Hz), 128.67, 126.11 (d, J = 21.5 Hz), 121.53 (q, J = 270.5 Hz), 116.79 (t, J = 268.5 Hz), 104.80, 36.23, 24.63. HRMS (ESI) calculated for C19H13Cl2F5N3OS [M+H]+ 527.9566 and found to be 527.9562.

3-chloro-2-(4-(((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)thio)phenyl)-5-fluoropyridine (6c): Yellow solid; Yield 67.1%; M.p. 74.3–76.6 °C. 1H NMR (400 MHz, DMSO-d6) δ: 8.70 (d, J = 2.6 Hz, 1H), 8.22 (dd, J = 8.5, 2.5 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.48 – 7.43 (m, 2H), 7.30 (t, J = 7.1 Hz, 1H), 4.15 (s, 2H), 3.79 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ: 156.86 (d, J = 21.1 Hz), 151.96 (d, J = 4.0 Hz), 143.69 (t, J = 3.7 Hz), 137.48 (q, J = 37.1 Hz), 136.96 (d, J = 5.4 Hz), 136.71, 135.58, 130.35, 129.59 (d, J = 4.6 Hz), 128.67, 126.11 (d, J = 21.5 Hz), 121.53 (q, J = 270.5 Hz), 116.79 (t, J = 268.5 Hz), 104.80, 36.23, 24.63. HRMS (ESI) calculated for C19H13ClF5N3OS [M+H]+ 468.0367 and found to be 468.0368.

5-chloro-2-(4-(((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)thio)phenyl)-5-trifluoromethylpyridine (6d): Yellow solid; Yield 81.2%; M.p. 79.9–82.5 °C. 1H NMR (400 MHz, DMSO-d6) δ: 8.63 (s, 1H), 8.20 (d, J = 10.9 Hz, 1H), 7.88 (d, J = 7.7 Hz, 2H), 7.50 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.14 Hz, 1H), 4.16 (s, 2H), 3.79 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ: 156.26 (d, J = 265.6 Hz), 144.42 (d, J = 4.6 Hz), 143.22, 142.85 (d, J = 10.3 Hz), 137.68, 137.03 (q, J = 37.3 Hz), 131.84 (d, J = 5.9 Hz), 129.96 (d, J = 3.8 Hz), 128.93 (d, J = 6.2 Hz), 128.42, 125.09 (d, J = 23.9 Hz), 121.07 (q, J = 270.3 Hz), 116.33 (t, J = 268.5 Hz), 104.28, 35.79, 23.98. HRMS (ESI) calculated for C19H13ClF5N3OS [M+H]+ 468.0367 and found to be 468.0366.

3-chloro-2-(4-(((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)thio)phenyl)-5-methylpyridine (6e): Yellow solid; Yield 79.0%; M.p. 106.4–108.7 °C. 1H NMR (400 MHz, DMSO-d6) δ: 8.47 (s, 1H), 7.89 (s, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.30 (t, J = 71.5 Hz, 1H), 4.14 (s, 2H), 3.79 (s, 3H), 2.35 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ: 151.78, 148.43, 143.24 (t, J = 3.8 Hz), 138.44, 137.03 (q, J = 37.1 Hz), 136.08, 135.94, 134.06, 129.88, 128.48, 128.26, 121.08 (q, J = 270.6 Hz), 116.35 (t, J = 268.4 Hz), 104.41, 35.78, 24.27, 17.03. HRMS (ESI) calculated for C19H16ClF5N3OS [M+H]+ 464.0617 and found to be 464.0617.
3-chloro-2-((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)sulfonyl)phenyl)pyridine (7f): White solid; Yield 80.7%; M.p. 116.9–119.8 °C. 1H NMR (400 MHz, DMSO-d$_6$) δ: 8.29 (s, 1H), 8.16 (s, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 4.56 (s, 2H), 3.80 (s, 3H), 3.28 (s, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ: 157.16 (d, J = 266.8 Hz), 145.30 (t, J = 4.6 Hz), 142.20 (d, J = 8.5 Hz), 139.78 (d, J = 5.8 Hz), 139.04, 138.60 (q, J = 37.2 Hz), 131.92 (d, J = 4.2 Hz), 129.86 (d, J = 6.2 Hz), 129.02, 125.96 (d, J = 23.9 Hz), 121.06 (q, J = 270.5 Hz), 117.07 (t, J = 267.3 Hz), 96.62, 49.97, 36.48. HRMS (ESI): calculated for C$_{18}$H$_2$ClF$_6$N$_3$O$_7$Na [M+Na]$^+$ 522.0084 and found to be 522.0085.

3-chloro-2-((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)sulfonyl)phenyl)pyridine (7e): White solid; Yield 95.0%; M.p. 106.8–109.2 °C. 1H NMR (400 MHz, DMSO-d$_6$) δ: 8.72 (d, J = 1.1 Hz, 1H), 8.30 (dd, J = 11.0, 1.9 Hz, 1H), 8.16 (d, J = 7.4 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 4.56 (s, 2H), 3.80 (s, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ: 157.16 (d, J = 266.8 Hz), 145.30 (t, J = 4.6 Hz), 142.20 (d, J = 10.5 Hz), 139.78 (d, J = 5.8 Hz), 139.04, 138.60 (q, J = 37.2 Hz), 131.92 (d, J = 4.2 Hz), 129.86 (d, J = 6.2 Hz), 129.02, 125.96 (d, J = 23.9 Hz), 121.06 (q, J = 270.5 Hz), 117.07 (t, J = 267.3 Hz), 96.62, 49.97, 36.48. HRMS (ESI): calculated for C$_{18}$H$_2$ClF$_6$N$_3$O$_7$Na [M+Na]$^+$ 522.0084 and found to be 522.0085.

3-chloro-2-((5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl)sulfonyl)phenyl-5-methylpyridine (7e): White solid; Yield 80.7%; M.p. 116.9–119.8 °C. 1H NMR (400 MHz, DMSO-d$_6$) δ: 8.53 (s, 1H), 7.97 (s, 1H), 7.95 – 7.85 (m, 4H), 7.26 (t, J = 7.8 Hz, 1H), 4.56 (s, 2H), 3.80 (s, 3H), 2.39 (s, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ: 151.36, 149.13, 145.29 (t, J = 3.2 Hz), 143.80, 139.03, 138.61 (q, J = 37.5 Hz), 138.24, 135.60, 130.75, 129.27, 128.42, 121.08 (q, J = 269.3 Hz), 117.10 (t, J = 267.3 Hz), 96.68, 49.97, 36.47, 17.57. HRMS (ESI): calculated for C$_{18}$H$_2$ClF$_6$N$_3$O$_7$Na [M+Na]$^+$ 518.0335 and found to be 518.0337.

3.3. Herbicial Activity Test

Levels of herbicidal activity for compounds 6a–6c and 7a–7e against the monocotyledonous weeds Digitaria sanguinalis (DS), Echinochloa crusgalli (EC), and Setaria viridis (SV), and the dicotyledonous weeds Abutilon theophrasti (AT), Amaranthus retroflexus (AR), and Eclipta prostrate (EP) were determined using previously disclosed methods [32], with the results being listed in Table 1.

4. Conclusions

In conclusion, 10 novel pyrazole derivatives containing phenylpyridine moieties were prepared using pyroxsulfone as the lead compound. Among these, compounds 6a and 6c possessed moderate activity (50%) against EP for post-emergence at 150 g a.i./hm$^2$, which was slightly superior to pyroxsulfone. This study suggested that it may be the introduction of the phenylpyridine structure that allowed the target compounds to exhibit herbicidal
activity at post-emergence only. Thus, compounds 6a and 6c may be lead compounds for further structural optimization.

**Supplementary Materials:** The following supporting information is available online at: https://www.mdpi.com/article/10.3390/molecules27196274/s1. Figure S1–30: 1H NMR, 13C NMR, and HRMS spectra of target compounds 6a–6e and 7a–7e.

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**Samples Availability:** Samples of the compounds are not available from authors.

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