新規なアシルチオウレアおよび2H‐1,2,4‐チアジアゾロ[2,3‐α]ピリミジン類の合成と植物毒性

誌名	Journal of pesticide science
ISSN	1348589X
著者名	Wang,M.
発行元	日本農薬学会
巻/号	37巻1号
巻号補足	
掲載ページ	p. 15-19
発行年月	2012年2月

J. Pestic. Sci. **37**(1), 15–19 (2012)
DOI: 10.1584/jpestics.G11-02

Original Article

Synthesis and phytotoxic activity of novel acylthiourea and 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidine derivatives

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(Received January 17, 2011; Accepted February 18, 2011)

Eight *N*-[3-(2,4-dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-*N'*-(4,6-disubstituted pyrimidin-2-yl)thioureas and eight 5,7-disubstituted-2-[3-(2,4-dichlorophenyl)-5-methyl isoxazol-4-ylcarbonylimino]-2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidines were synthesized by multi-step reactions in yields of 50–85%. The structures of the target compounds were confirmed by IR, ^{1}H NMR spectra and elemental analyses. Phytotoxic activities against *Echinochloa crus-galli* L., *Digitaria ciliaris* L., *Brassica napus* L. and *Chenopodium serotinum* L. were evaluated by the culture dish method. Preliminary bioassay results indicated that some target compounds exhibited good phytotoxic activity at a dose of 100 mg/L, with an inhibitory rate of 76.0–85.6% on root growth, even higher than the control herbicide, fenoxaprop-P-ethyl. © Pesticide Science Society of Japan

Keywords: acylthiourea, thiadiazolo[2,3-α]pyrimidine, synthesis; phytotoxic activity.

Introduction

Heterocyclic acylthioureas exhibit excellent biological activities, such as fungicidal,[1] insecticidal,[2] antitumor[3] and regulation of plant growth,[4] and some acylthioureas containing 4,6-disubstitued pyrimidinyl possess herbicidal activity.[5] Additionally, *N*-4,6-disubstitued pyrimidinyl acylthiourea can be transformed into fused heterocyclic derivative (*e.g.* 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidine) in the presence of bromine,[6] and the derivative displays high herbicidal activity. For example, 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidines containing 2,4-dichlorophenoxy,[7] show excellent herbicidal activity against both *Echinochloa crusgalli* L. and *Amaranthus retroflexus* L. at 1.5 kg/ha. Currently, considerable attention is directed toward the discovery and development of novel 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidine herbicides.

On the other hand, many isoxazole compounds have been developed into herbicides, fungicides, insecticides and other agricultural chemicals.[8–10] In particular, their excellent herbicidal activity attracts many pesticide chemist's attention, and more than ten isoxazole herbicides have been discovered, such as oxadiazon,[11] isoxaflutole,[12] and isoxapyrifop.[13] Furthermore, it is well known that 2,4-dichlorophenyl moiety is employed in herbicidal agents,[14] for example, pyrazolate,[15] dichlofop-methyl[16] and chlomethoxynil[17] have been designed and screened as commercial herbicides.

However, up to now, acylthiourea and 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidine containing isoxazole and 2,4-dichlorophenyl moieties have not been reported. Motivated by the above findings, and in a continuation of our interest in the synthesis of many heterocyclic systems for a biological screening program in our laboratory,[18] we have designed and synthesized a series of novel acylthioureas and 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidines containing isoxazole and 2,4-dichlorophenyl moieties. Their herbicidal activities have been evaluated against selected weeds, and the result shows that some target compounds possess good phytotoxic activity. The synthetic pathway is shown in Scheme 1.

Materials and Methods

1. Instruments and reagents

Melting points were recorded on an X-5 microscopic melting point apparatus and are uncorrected. ^{1}H NMR spectra were performed in DMSO-d_6 solvent on a Varian Mercury Plus 400 spectrophotometer using tetramethylsilane as an internal standard. IR spectra were recorded on a Nicolet-380 infrared spectrophotometer. Elemental analyses were carried out using a Vario EL III Elemental Analyzer. Ultrasound irradiation was conducted using a KQ-250 ultrasonic cleaner.

3-(2,4-Dichlorophenyl)-5-methylisoxazole-4-formyl chloride (**1**) was prepared according to the reference,[19] and 3-(2,4-dichlorophenyl)-5-methylisoxazole-4-formyl isothiocyanate (**2**) was synthesized from **1**.[20] 2-Amino-4,6-disubstitu-

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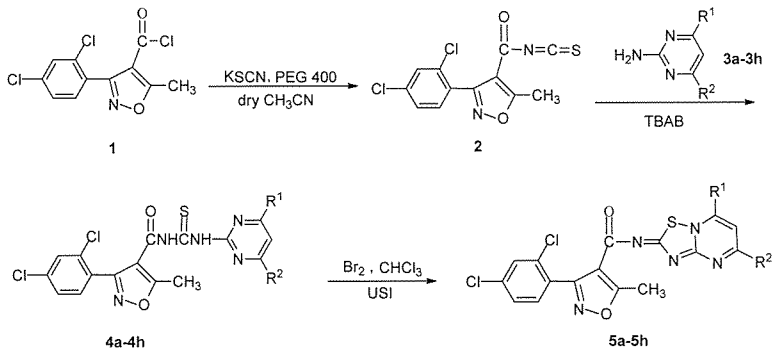
Published online January 6, 2012



Scheme 1. Synthetic pathway of the target compounds **4** and **5**.

ented pyrimidines (**3**) were prepared following the reference.[21] Acetonitrile was dehydrated, thionyl chloride was distilled, and potassium thiocyanate was dried in a vacuum before use.

2. Chemical synthesis

General procedure for synthesizing compounds **4a–4h**[22]: To a stirred solution of 2-amino-4,6-disubstituted pyrimidine **3** (5 mmol) and a catalytic amount of tetrabutyl ammonium bromide (TBAB, 0.10 g) in dry acetonitrile (10 mL) was added dropwise a mixture of 3-(2,4-dichlorophenyl)-5-methylisoxazole-4-formyl isothiocyanate **2** (1.56 g, 5 mmol) in dry acetonitrile (10 mL) at room temperature within 0.5 hr. The mixture was then refluxed with stirring for 2 hr. After evaporation of the solvent under reduced pressure, the residue was cooled to room temperature to give a solid, which was purified by recrystallization from a solution of ethanol and water, or by flash column chromatography on silica gel eluted with ethyl acetate: petroleum ether (1:2–1:4, by volume) to afford compounds **4a–4h** as white or yellow powders.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4,6-dimethylpyrimidin-2-yl)thiourea* ***(4a)***. Yield: 78.6%. Mp: 138–140°C. IR ν_{max} (KBr) cm^{-1}: 3372, 3175, 1715, 1609, 1283. ^1H NMR δ_H (DMSO-d_6): 2.50 (s, 6H, Pyrim-CH_3), 2.72 (s, 3H, Isoxazol-CH_3), 7.03 (s, 1H, Pyrim-H), 7.63–7.86 (m, 3H, Ph-H), 11.56 (s, 1H, NH), 12.72 (s, 1H, NH). Anal. Found: C, 49.46; H, 3.35; N, 16.01%. Calcd. For $C_{18}H_{15}Cl_2N_5O_2S$: C, 49.55; H, 3.47; N, 16.05%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4-hydroxy-6-methylpyrimidin-2-yl)thiourea* ***(4b)***. Yield: 64.2%. Mp: 236–237°C. IR ν_{max} (KBr) cm^{-1}: 3308, 3166, 1698, 1609, 1286. ^1H NMR δ_H (DMSO-d_6): 2.08 (s, 3H, Pyrim-CH_3), 2.50 (s, 3H, Isoxazol-CH_3), 5.60 (s, 1H, Pyrim-H), 7.71–7.93 (m, 3H, Ph-H), 11.75 (s, 1H, NH). Anal. Found: C, 46.09; H, 2.89; N, 15.86%. Calcd. For $C_{17}H_{13}Cl_2N_5O_3S$: C, 46. 59; H, 2.99; N, 15.98%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4-chloro-6-methylpyrimidin-2-yl)thiourea* ***(4c)***. Yield: 50.2%. Mp: 184–186°C. IR ν_{max} (KBr) cm^{-1}: 3372, 3114, 1695, 1609, 1283. ^1H NMR δ_H (DMSO-d_6): 2.52 (s, 3H, Pyrim-CH_3), 2.64 (s, 3H, Isoxazol-CH_3), 6.52 (s, 1H, Pyrim-H), 7.54–8.17 (m, 3H, Ph-H), 10.88 (s, 1H, NH). Anal. Found: C, 45.43; H, 3.07; N, 15.06%. Calcd. For $C_{17}H_{12}Cl_3N_5O_2S$: C, 44.70; H, 2.65; N, 15.33%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4-methoxy-6-methylpyrimidin-2-yl)thiourea* ***(4d)***. Yield: 55.3%. Mp: 150–152°C. IR ν_{max} (KBr) cm^{-1}: 3372, 3141, 3065, 1705, 1609, 1283. ^1H NMR δ_H (DMSO-d_6): 2.53 (s, 3H, Pyrim-CH_3), 2.73 (s, 3H, Isoxazol-CH_3), 3.32 (s, 3H, Pyrim-OCH_3), 7.30–7.47 (m, 3H, Ph-H), 7.61(s, 1H, Pyrim-H), 8.74 (s, 1H, NH), 12.80 (bs, 1H, NH). Anal. Found: C, 47.65; H, 3.29; N, 15.09%. Calcd. For $C_{18}H_{15}Cl_2N_5O_3S$: C, 47.80; H, 3.34; N, 15. 48%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4-methyl-6-methylthiopyrimidin-2-yl)thiourea* ***(4e)***. Yield: 53.7%. Mp: 156–158°C. IR ν_{max} (KBr) cm^{-1}: 3372, 3125, 1697, 1594, 1241. ^1H NMR δ_H (DMSO-d_6): 2.29 (s, 3H, Pyrim-CH_3), 2.50 (s, 3H, Pyrim-SCH_3), 2.77 (s, 3H, Isoxazol-CH_3), 6.44 (s, 1H, Pyrim-H), 7.70–7.88 (m, 3H, Ph-H), 11.61(s, 1H, NH), 12.72 (s, 1H, NH). Anal. Found: C, 45.44; H, 3.86; N, 15.67%. Calcd. For $C_{18}H_{15}Cl_2N_5O_2S_2$: C, 46.16; H, 3.23; N, 14.95%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4-chloro-6-methoxypyrimidin-2-yl)thiourea* ***(4f)***. Yield: 65.9%. Mp: 175–176°C. IR ν_{max} (KBr) cm^{-1}: 3365, 3170, 1691, 1605, 1290. ^1H NMR δ_H (DMSO-d_6): 2.71 (s, 3H, Isoxazol-CH_3), 3.84 (s, 6H, Pyrim-OCH_3), 5.99 (s, 1H, Pyrim-H), 7.63–8.09 (m, 3H, Ph-H), 9.2 (bs, 1H, NH), 12.6(bs, 1H, NH). Anal. Found: C, 43.12; H, 2.61; N, 14.91%. Calcd. For $C_{17}H_{12}Cl_3N_5O_3S$: C, 43.19; H, 2.56; N, 14.81%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-N′-(4,6-dimethoxypyrimidin-2-yl)thiourea* ***(4g)***. Yield: 76.7%. Mp: 156–157°C. IR ν_{max} (KBr) cm^{-1}: 3307, 3113, 1650, 1560, 1229. ^1H NMR δ_H (DMSO-d_6): 2.65 (s, 3H, Isoxazol-CH_3), 3.92 (s, 6H, Pyrim-OCH_3), 5.55 (s, 1H, Pyrim-H), 7.90–7.92 (m, 3H, Ph-H), 10.94 (s, 1H, NH). Anal. Found: C, 47.65; H, 3.26; N, 14.99%. Calcd. For $C_{18}H_{15}Cl_2N_5O_4S$: C, 47.80; H, 3.34; N, 15.49%.

N-*[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-*

N′-(4-methoxy-6-methylthiopyrimidin-2-yl)thiourea (**4h**). Yield: 65.3%. Mp: 142–144°C. IR ν_{max} (KBr) cm^{-1}: 3374, 3141, 1692, 1592, 1240. ^1H NMR δ_H (DMSO-d_6): 2.50 (s, 3H, Pyrim-SCH_3), 2.75 (s, 3H, Isoxazol-CH_3), 3.91 (s, 3H, Pyrim-OCH_3), 5.81(s, 1H, Pyrim-H), 7.26–7.53 (m, 3H, Ph-H). Anal. Found: C, 44.66; H, 3.24; N, 14.13%. Calcd. For $C_{18}H_{15}Cl_2N_5O_3S_2$: C, 44.63; H, 3.12; N, 14.46%.

General procedure for synthesizing compounds **5a–5h**[7]: To a solution of *N*-[3-(2,4-dichlorophenyl)-5-methylisoxazol-4-ylcarbonyl]-*N′*-(4,6-disubstituted pyrimidin-2-yl)thiourea **4** (2 mmol) in chloroform (10 mL) was added dropwise a mixture of bromine (0.32 g, 2 mmol) in chloroform (10 mL) within 0.5 hr while stirring in an ice-bath. The mixture was then sonicated (250 W) at room temperature in an ultrasonic cleaner for 1–2 hr. TLC was employed to monitor the progress of the reaction. The resulting mixture was left for one night and the precipitate was filtered, washed, dried and recrystallized from anhydrous acetonitrile to afford compounds **5a–5h** as yellow or yellowish powders.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-5,7-dimethyl-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5a**). Yield: 75.6%. Mp: 199–201°C. IR ν_{max} (KBr) cm^{-1}: 1680, 1609. ^1H NMR δ_H (DMSO-d_6): 2.66 (s, 3H, Pyrim-CH_3), 2.72 (s, 3H, Pyrim-CH_3), 2.99 (s, 3H, Isoxazol-CH_3), 6.84 (s, 1H, Pyrim-H), 7.26–7.42 (m, 3H, Ph-H). Anal. Found: C, 49.75; H, 3.03; N, 15.99%. Calcd. For $C_{18}H_{13}Cl_2N_5O_2S$: C, 49.78; H, 3.02; N, 16.13%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-7-hydroxy-5-methyl-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5b**). Yield: 80.0%. Mp: >300°C. IR ν_{max} (KBr) cm^{-1}: 1660, 1597. ^1H NMR δ_H (DMSO-d_6): 2.50 (s, 3H, Pyrim-CH_3), 2.82 (s, 3H, Isoxazol-CH_3), 5.90 (s, 1H, Pyrim-H), 7.39–7.52 (m, 3H, Ph-H). Anal. Found: C, 46.75; H, 3.05; N, 15.97%. Calcd. For $C_{17}H_{11}Cl_2N_5O_3S$: C, 46.99. H, 2.78; N, 16.09%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-5-chloro-7-methyl-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5c**). Yield: 76.8%. Mp: 232–234°C. IR ν_{max} (KBr) cm^{-1}: 1670, 1590. ^1H NMR δ_H (DMSO-d_6): 2.50 (s, 3H, Pyrim-CH_3), 2.72 (s, 3H, Isoxazol-CH_3), 5.84 (s, 1H, Pyrim-H), 7.42–7.58 (m, 3H, Ph-H). Anal. Found: C, 44.85; H, 2.25; N, 15.51. Calcd. For $C_{17}H_{10}Cl_3N_5O_2S$: C, 44.90; H, 2.22; N, 15.40%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-7-methoxy-5-methyl-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5d**). Yield: 85.3%. Mp: 220–221°C. IR ν_{max} (KBr) cm^{-1}: 1640, 1605. ^1H NMR δ_H (DMSO-d_6): 2.50 (s, 3H, Pyrim-CH_3), 2.62 (s, 3H, Isoxazol-CH_3), 3.92 (s, 3H, Pyrim-OCH_3), 6.75 (s, 1H, Pyrim-H), 7.39–7.57 (m, 3H, Ph-H). Anal. Found: C, 48.25; H, 3.05; N, 15.51%. Calcd. For $C_{18}H_{13}Cl_2N_5O_3S$: C, 48.01; H, 2.91; N, 15.55%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-5-methyl-7-methylthio-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5e**). Yield: 82.1%. Mp: 222–224°C. IR ν_{max} (KBr pellet) cm^{-1}: 1650, 1610. ^1H NMR δ_H (DMSO-d_6): 2.26 (s, 3H, Pyrim-CH_3), 2.50 (s, 3H, Pyrim-SCH_3), 2.72 (s, 3H, Isoxazol-CH_3), 5.75 (s, 1H, Pyrim-H), 7.43–7.67 (m, 3H, Ph-H). Anal. Found: C, 46.35; H, 2.75; N, 15.01%. Calcd. For $C_{18}H_{13}Cl_2N_5O_2S_2$: C, 46.36; H, 2.81; N, 15.02%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-5-chloro-7-methoxy-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5f**). Yield: 79.6%. Mp: 235–236°C. IR ν_{max} (KBr) cm^{-1}: 1650, 1597. ^1H NMR δ_H (DMSO-d_6): 2.72 (s, 3H, Isoxazol-CH_3), 3.95 (s, 3H, Pyrim-OCH_3), 6.65 (s, 1H, Pyrim-H), 7.32–7.55 (m, 3H, Ph-H). Anal. Found: C, 43.25; H, 2.15; N, 15.01%. Calcd. For $C_{17}H_{10}Cl_3N_5O_3S$: C, 43.38; H, 2.14; N, 14.88%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-5,7-dimethoxy-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5g**). Yield: 77.3%. Mp: 213–214°C. IR ν_{max} (KBr) cm^{-1}: 1650, 1609. ^1H NMR δ_H (DMSO-d_6): 2.72 (s, 3H, Isoxazol-CH_3), 3.80 (s, 3H, Pyrim-OCH_3), 3.90 (s, 3H, Pyrim-OCH_3), 5.25 (s, 1H, Pyrim-H), 7.29–7.58 (m, 3H, Ph-H). Anal. Found: C, 46.35; H, 2.85; N, 15.01%. Calcd. For $C_{18}H_{13}Cl_2N_5O_4S$: C, 46.36; H, 2.81; N, 15.02%.

2-[3-(2,4-Dichlorophenyl)-5-methylisoxazol-4-ylcarbonylimino]-7-methoxy-5-methylthio-2H-1,2,4-thiadiazolo[2,3-α]pyrimidine (**5h**). Yield: 83.9%. Mp: 208–210°C. IR ν_{max} (KBr) cm^{-1}: 1680, 1597. ^1H NMR δ_H (DMSO-d_6): 2.50 (s, 3H, Pyrim-SCH_3), 2.72 (s, 3H, Isoxazol-CH_3), 3.82 (s, 3H, Pyrim-OCH_3), 5.15 (s, 1H, Pyrim-H), 7.34–7.68 (m, 3H, Ph-H). Anal. Found: C, 44.85; H, 2.75; N, 14.51%. Calcd. For $C_{18}H_{13}Cl_2N_5O_3S_2$: C, 44.82; H, 2.72; N, 14.52%.

3. *Herbicidal activity assays*

The *in vitro* herbicidal activities of target compounds **4** and **5** were evaluated with monocotyledon plants (*Digitaria ciliaris* L. *and Echinochloa crus-galli* L.) and dicotyledon plants (*Brassica napus* L. *and Chenopodium serotinum* L.).[23] The tested compound was dissolved in *N,N*-dimethyl formamide (0.5 mL) with the addition of Tween 80 (0.4 mg) and diluted with distilled water to give the tested solutions of specific concentrations (100 and 10 mg/L). The seeds were germinated at 27±1°C, with 24 hr photoperiod and 80% relative humidity, and then every 10 germinated seeds were placed in a culture dish covered with 2 pieces of filter paper. The culture dishes were kept under the same conditions for 72 hr. Moreover, fenoxaprop-P-ethyl, a commercial herbicide and more active to monocotyledon plants, was used as a control, and the emulsion which did not contain the tested compound as a blank, respectively. Three replicates were performed in each

Table 1. Synthesis of **5a–5c** under both ultrasonic irradiation and conventional methods

No.	Ultrasonic irradiation		Conventional	
	Time (min)	Yield (%)	Time (min)	Yield (%)
5a	90	85	180	54
5b	110	83	270	50
5c	120	80	360	53

treatment. The results, expressed as the mean values obtained in three independent experiments, are presented in Table 2. The inhibitory rate was calculated according to the following formula:

$$\text{Inhibitory rate (\%)} = (L_0 - L_1)/L_0 \times 100\%$$

In which L_0 is the length of root in the blank test, and L_1 is the length of root in the presence of tested compounds.

Results and Discussion

1. Synthesis

In the synthesis of compounds **4** and **5**, ultrasound irradiation was tested in order to improve the synthetic methods. It was found that the use of ultrasound irradiation could afford compound **5** in a shorter time and in better yield. The results of **5a–5c** are shown in Table 1.

The structures of the newly synthesized compounds were assigned on the basis of ^{1}H NMR, IR and elemental analyses. In IR spectra, compound **4** showed absorption bands around 3300 and 3100 cm^{-1}, respectively, originating from N–H stretching vibration. The strong bands around 1710–1650 cm^{-1} could be assigned to the C=O stretching vibration, and 1610–1590 cm^{-1} to the C=N stretching vibration, while 1290–1240 cm^{-1} were owing to the vibration of C=S. In the ^{1}H NMR spectra, the singlet signal around 2.70 ppm was attributed to the CH_3 protons on the isoxazole ring, while the singlet signal near to 6.45 ppm was assigned to the proton on the pyrimidine ring. Two singlet peaks in the range of 13.52–12.76 and 11.71–11.36 ppm were due to the presence of N–H in the thiourea bridge. However, only one or even no signal of N–H appeared in some target compounds, due to the intramolecular hydrogen bond of O···H–N forming a six-number ring and a solvation effect between acyl thioureas and deuterated solvent.[24)]

In compounds **5**, the C=O band significantly moved to lower frequencies (1680–1640 cm^{-1}). Cyclization of **4** to fused heterocyclic 2*H*-1,2,4-thiadiazolo[2,3-α]pyrimidine **5** was monitored by IR spectra where the thioamide peak disappeared in the regions of 3300–3100 cm^{-1} and 1290–1240 cm^{-1}, which was also confirmed by the vanishing of signals around 8.75–12.76 ppm in ^{1}H NMR.

2. Phytotoxic activity

As seen from Table 2, **4a**, **4d** and **4g** exhibited moderate activities against the four tested plants at a dose of 100 mg/L, with an inhibitory rate of 60.2–73.6%. On the other hand, **4e** displayed high activity against *Brassica napus* L. and *Chenopodium serotinum* L. at the same dose, and the inhibitory rate was

Table 2. Phytotoxic activities of compounds **4** and **5** against the roots off our tested plants (*in vitro*)

No.	R^1	R^2	Inhibitory rate (%)[a)]							
			Dig.		*Ech.*		*Bra.*		*Che.*	
			100 mg/L	10 mg/L	100 mg/L	10 mg/L	100 mg/L	10 mg/L	100 mg/L	10 mg/L
4a	CH_3	CH_3	61.4	26.5	64.7	18.5	68.0	16.1	65.4	16.9
4b	OH	CH_3	49.3	−6.24	46.8	−9.78	52.3	6.7	46.7	−5.86
4c	CH_3	Cl	44.2	10.2	48.7	−6.84	50.8	8.36	48.3	28.9
4d	OCH_3	CH_3	60.2	30.2	61.8	12.3	69.3	15.7	59.8	15.3
4e	SCH_3	CH_3	45.5	26.7	47.1	27.4	73.6	42.4	86.1	32.8
4f	OCH_3	Cl	62.2	14.6	56.3	18.5	61.0	30.7	53.2	21.9
4g	OCH_3	OCH_3	65.9	32.0	60.9	21.8	70.8	35.2	78.6	30.7
4h	OCH_3	SCH_3	55.6	34.8	40.9	19.3	69.2	18.7	60.3	−8.31
5a	CH_3	CH_3	84.9	15.2	76.0	25.2	76.8	46.3	76.9	26.7
5b	OH	CH_3	72.1	30.1	65.8	30.5	79.2	38.5	59.3	32.9
5c	CH_3	Cl	68.1	32.8	55.6	25.8	70.2	20.1	73.6	18.6
5d	OCH_3	CH_3	80.6	50.3	80.5	30.9	80.6	26.4	80.4	45.7
5e	SCH_3	CH_3	70.6	26.8	75.4	37.5	62.8	32.8	75.2	21.9
5f	OCH_3	Cl	72.8	16.5	40.8	10.8	70.8	28.6	65.9	19.3
5g	OCH_3	OCH_3	85.3	53.8	85.6	43.2	85.6	49.3	82.7	28.9
5h	OCH_3	SCH_3	79.6	19.8	55.6	21.4	75.8	27.4	68.3	23.8
CK[b)]			85.6	35.7	71.8	58.4	42.2	16.4	48.7	16.8

[a)] *Dig.*, *Digitaria sanguinalis* L.; *Ech.*, *Echinochloa crus-galli* L.; *Bra.*, *Brassica napus* L.; *Che.*, *Chenopodium serotinum* L. [b)] CK, Commercial herbicide fenoxaprop-P-ethyl.

86.1% and 73.6%, respectively, while its inhibitory rates against *Echinochloa crus-galli* L. *and Digitaria ciliaris* L. were only 47.1% and 45.5%, respectively, which means that it demonstrated selectivity for dicotyledon plants.

Similarly, **5a**, **5d** and **5g** possessed high activity against the four tested plants at a dose of 100 mg/L, with an inhibitory rate of 76.0–85.6%, all higher than that of fenoxaprop-P-ethyl; however, both compounds **4** and **5** exhibited lower herbicidal activity at a dose of 10 mg/L. In summary, compound **5** showed higher phytotoxic activity than compound **4**.

By analyzing the relationship between molecular structure and activity, it was found that the compound, in which both R^1 and R^2 are OCH_3 or CH_3, or one is OCH_3 and the other is CH_3, possesses relatively high phytotoxic activity.

Acknowledgments

Thanks go to Prof. Wang Jin-Xin from the College of Plant Protection in Shandong Agricultural University for his contributions to the Phytotoxic bioassay.

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報　文

新規なアシルチオウレアおよび2*H*-1,2,4-チアジアゾロ[2,3-α]ピリミジン類の合成と植物毒性

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新規な*N*-アシル-*N*′-(4,6-置換ピリミジニル）チオウレア類と2*H*-1,2,4-チアジアゾロ[2,3-α]ピリミジン類を，収率50〜85%で合成した．それらの構造は，IR, ^{1}H NMRおよび元素分析により確認した．イヌビエ，メヒシバ，セイヨウアブラナ，コアカザに対する除草活性（植物毒性）をシャーレ試験により評価した．その結果，数種の化合物が良好な除草活性（植物毒性）を有しており，100 mg/Lの濃度で対照薬剤のフェノキサプロップ-P-エチルより高い76.0〜85.6%の根部伸長抑制率を示した．

（文責：編集事務局）