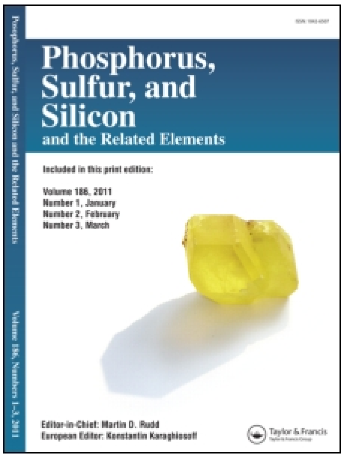

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Synthesis and Herbicidal Activity of O,O-Diethyl N-{4-Methyl-[1,2,3]thiadiazole-5-carbonyl}- 1-amino-1-substitutedbenzyl Phosphonates

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SYNTHESIS AND HERBICIDAL ACTIVITY OF O,O-DIETHYL N-{4-METHYL-[1,2,3]THIADIAZOLE-5-CARBONYL}-1-AMINO-1-SUBSTITUTEDBENZYL PHOSPHONATES

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Target compounds 3 were synthesized by the condensation of O,O-diethyl α-amino substitutedbenzyl phosphonates 1 and 4-methyl-[1,2,3]thiadiazole-5-carboxylic acid 2 in the presence of dicyclohexylcarbodiimide (DCC) as a dehydration reagent. Their structures were confirmed by spectroscopic data (IR, ^{1}H NMR, ^{31}P NMR, MS) and elemental analysis. The results of a preliminary bioassay (in vitro) indicated that some of the title compounds 3 possessed moderate to good herbicidal activities against dicotyledonous plants (**Brassica campestris L*****) at the concentration of 100 mg/L, and most of these compounds exhibited higher herbicidal activities against dicotyledonous plants (*****Brassica campestris L*****) than monocotyledonous plants (*****Echinochloa crus-galli*****).***

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Amide; α-amino substitutedbenzyl phosphonate; herbicidal activity; [1,2,3]thiadiazole

INTRODUCTION

α-Amino phosphonic acids and their ester derivatives, as bioisosteres of natural amino acids, are receiving increasing attention in medicinal chemistry and pesticide science because some derivatives have been found to exhibit a wide range of biological activities such as enzyme inhibition, antibiotics, and haptens of catalytic antibodies, fungicides, herbicides, plant regulators, and plant virucides [for example, as antiviral agents against tobacco mosaic virus (TMV)].[1–8] Elictor is a kind of environment-benign novel agrochemical that protects crops against pathogen attack by promoting their immune system. [1,2,3]Thiadiazole chemistry has attracted more and more attention[9]; some thiadiazole derivatives have

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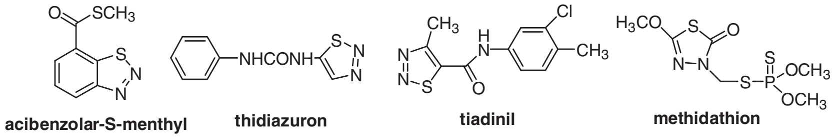
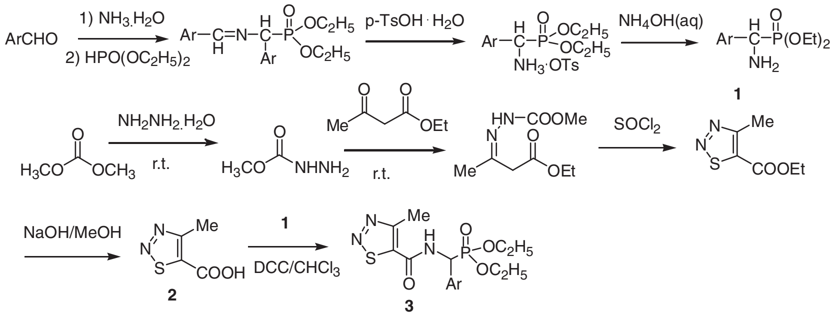


Figure 1 Structures of some commercial thiadiazole pesticides.

played a major role in modern pesticidal industry and have been commercialized as plant activators, fungicides, plant growth regulators, and insecticides in plant protection[10,11] (see Figure 1). For example, acibenzolar-S-methyl was developed by Syngenta and used as plant activator; tiadinil was discovered by Nihon Nohyaku and acted as a plant activator, which induces fungicide resistance in rice plants; thidiazuron was used as plant growth regulator; methidathion was developed and used cholinesterase inhibitor, which acts as a nonsystemic insecticide and acaricide with contact and stomach action. In an attempt to find novel agrochemical lead compounds, we have synthesized a series of title compounds **3** by the condensation of O,O-diethyl α-amino substitutedbenzyl phosphonate **1** and 4-methyl-[1,2,3]thiadiazole-5-carboxylic acid **2** in the presence of dicyclohexylcarbodiimide (DCC) as a dehydration reagent, as shown in Scheme 1. The target compounds **3** were evaluated for herbicidal activities (see the Supplemental Materials, available online) *in vitro* against a dicotyledonous plant (*Brassica campestris L*) and a monocotyledonous plant (*Echinochloa crus-galli*).



Ar = C_6H_5(**3a**); 2-ClC_6H_4(**3b**); 4-ClC_6H_4(**3c**); 4-BrC_6H_4(**3d**); 4-$CH_3C_6H_4$(**3e**); 4-$CH_3OC_6H_4$(**3f**); 4-$NO_2C_6H_4$(**3g**); 2,4-$Cl_2C_6H_3$(**3h**)

Scheme 1 Synthesis route of the title compounds **3**.

RESULTS AND DISCUSSION

Synthesis and Structure Determination of Title Compounds 3

A series of novel O,O-diethyl N-{4-methyl-[1,2,3]thiadiazole-5-carbonyl}-1-amino-1-substitutedbenzyl phosphonates **3** was synthesized by the condensation of O,O-diethyl α-amino substitutedbenzyl phosphonate **1** with 4-methyl-[1,2,3]thiadiazole-5-carboxylic acid **2** in good yields in the presence of DCC as a dehydration reagent under mild conditions. The structures of target compounds **3** were deduced from their spectroscopic data (IR, ^{1}H NMR, ^{31}P NMR, MS) and elemental analysis. In the ^{1}H NMR spectra of **3**, the CH proton linking with the phosphonyl group displayed as a doublet of doublet due to coupling with P atom and nitrogen proton with chemical shifts in δ 5.6–6.2. The methyl protons linking with [1,2,3]thiadiazole ring presented as a singlet, giving chemical shifts in δ 2.8–2.9. Two methyl groups in the phosphonate moiety exhibited as two triplets and two methylene group as three multiple peaks due to their different chemical environments. For ^{31}P NMR spectra, the phosphorus atom of all compounds displayed as a singlet with chemical shifts in δ 17–21. The IR spectra of compounds **3** showed normal stretching absorption bands, indicating the existence of the NH ($\sim$3200 cm^{-1}), C=O ($\sim$1680 cm^{-1}), P=O ($\sim$1225 cm^{-1}), P—O—C ($\sim$1025 cm^{-1}) moieties. The EI-MS or ESI-MS of compounds **3** revealed the existence of their molecular ion peaks, which were in accordance with the given structures of products **3**.

Herbicidal Activities

The herbicidal activity values of the title compounds **3** against *Brassica campestris L* (oil rape) and *Echinochloa crus-galli* (barnyard grass) have been investigated at the concentrations of 100 mg/L and 10 mg/L compared with the commercially available herbicide, glyphosate, according to the method described in the Supplemental Materials.

EXPERIMENTAL

Instruments

The melting points of the products were determined on an XT-4 binocular microscope (Beijing Tech Instrument Co., Beijing, China) and were uncorrected. The IR spectra were recorded on a Nicolet NEXUS470 spectrometer as KBr pellets with absorption given in cm^{-1}. ^{1}H and ^{31}P NMR spectra were performed on a Varian Mercury Plus-600 (600 MHz) spectrometer at room temperature in $CDCl_3$ with TMS and 85% H_3PO_4 as the internal and external standards, respectively. Mass spectra were measured on a Finnigan TraceMS 2000 spectrometer at 70 eV using EI method or Applied Biosystems API 2000 LC/MS/MS (ESI-MS) spectrometer. Elemental analysis was taken on a Vario EL III elemental analysis instrument. Analytical TLC was performed on silica gel GF254. Unless otherwise noted, all materials were commercially available and were used directly without further purification. All solvents were dried and redistilled before use. α-Amino substitutedbenzyl phosphonates **1** were synthesized from aromatic aldehyde, ammonia, and diethyl phosphite according to the reported procedure.[12,13] 4-Methyl-[1,2,3]thiadiazole-5-carboxylic acid **2** was obatined in 78% yield using diethyl carbonate as the starting material, followed by nucleophilic substitution with 85% hydrazine hydrate, condensation with acetyl acetate, cyclization with $SOCl_2$, and then saponification according to the reported synthetic protocols.[14] Mp 174–176°C, lit. mp 173–175°C.

General Synthetic Procedures for O,O-Diethyl N-{4-Methyl-[1,2,3]-thiadiazole-5-carbonyl}-1-amino-1-substitutedbenzyl Phosphonates 3

To a solution of α-amino substitutedbenzyl phosphonate **1** (1.0 mmol) and 4-methyl-[1,2,3]thiadiazole-5-carboxylic acid **2** (0.14 g, 1.0 mmol) in anhydrous chloroform (5 mL), was added dropwise dicyclohexylcarbodiimide (DCC, 0.23 g, 1.1 mmol) in anhydrous chloroform (2 mL) at 0–5°C was added dropwise under stirring for 30 min. The mixture was allowed to stir at room temperature for 3–5 h (monitored by TLC). The solvent was removed under reduced pressure, acetone (2 mL) was added to the crude product, and the solid that formed was filtered off. Anhydrous ethyl ether (3 mL) was added to the filtrate, the product **3** was collected by filtration as colorless crystals in 71–94% yields.

Data for **3a**: Yield 72%, colorless crystals, mp 127–129°C; IR (KBr): υ 3209 (N—H), 1674 (C=O), 1546 (C=N), 1228 (P=O), 1028 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.05 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.34 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.80 (s, 3H, CH_3), 3.54–3.57 (m, 1H, OCH_2), 3.73–3.78 (m, 1H, OCH_2), 4.08–4.17 (m, 2H, OCH_2), 5.69 (dd, $J = 20.7$ Hz, $J = 9.6$ Hz, 1H, PCH), 7.34–7.36 (m, 3H, ArH), 7.54–7.56 (m, 2H, ArH), 9.00 (d, $J = 7.2$ Hz, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 18.76; EI-MS (70 eV): *m/z* 371 (17.6), 370 (19.4), 369 (M$^+$, 19.6), 368 (17.6), 226.5 (15.9), 225.5 (23.2), 177 (35.6), 173 (91.0), 171 (100), 169 (90.1), 142 (19.9), 105 (21.3), 104 (19.3), 91 (48.2), 90 (69.3), 77 (24.0). Anal. Calcd for $C_{15}H_{20}N_3O_4PS$: C 48.77, H 5.46, N 11.38; found C 48.35, H 5.10, N 11.53.

Data for **3b**: Yield 94%, colorless solid, mp 135–137°C; IR (KBr): υ 3214 (N—H), 1680 (C=O), 1541 (C=N), 1235 (P=O), 1022 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.06 (t, $J = 7.8$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.37 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.88 (s, 3H, CH_3), 3.62–3.65 (m, 1H, OCH_2), 3.83–3.86 (m, 1H, OCH_2), 4.17–4.22 (m, 2H, OCH_2), 6.24 (dd, $J = 21.3$ Hz, $J = 9.0$ Hz, 1H, PCH), 7.27–7.31 (m, 2H, ArH), 7.45 (t, $J = 7.2$ Hz, 1H, ArH), 7.68 (t, $J = 6.8$ Hz, 1H, ArH), 8.07 (s, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 17.52; ESI-MS: *m/z* 441.5 (M$^+$+K-1, 8%), 425.6 (M$^+$+Na-1, 22%), 403.5 (M$^+$, 100%). Anal. Calcd for $C_{15}H_{19}ClN_3O_4PS$: C 44.61, H 4.74, N 10.41; found C 44.50, H 4.47, N 10.36.

Data for **3c**: Yield 77%, colorless crystals, mp 153–155°C; IR (KBr): υ 3226 (N—H), 1667 (C=O), 1538 (C=N), 1234 (P=O), 1025 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.11 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.34 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.86 (s, 3H, CH_3), 3.68–3.71 (m, 1H, OCH_2), 3.87–3.90 (m, 1H, OCH_2), 4.09–4.18 (m, 2H, OCH_2), 5.60 (dd, $J = 21.3$ Hz, $J = 8.4$ Hz, 1H, PCH), 7.34 (d, $J = 7.8$ Hz, 2H, ArH), 7.45 (d, $J = 8.4$ Hz, 2H, ArH), 8.38 (sb, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 19.47; ESI-MS: *m/z* 425.5 (M$^+$+Na-1), 403.5 (M$^+$, 100%). Anal. Calcd for $C_{15}H_{19}ClN_3O_4PS$: C 44.61, H 4.74, N 10.41; found C 44.80, H 4.97, N 10.73.

Data for **3d**: Yield 79%, colorless crystals, mp 156–157°C; IR (KBr): υ 3218 (N—H), 1672 (C=O), 1535 (C=N), 1239 (P=O), 1021 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.12 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.34 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.83 (s, 3H, CH_3), 3.66–3.68 (m, 1H, OCH_2), 3.83–3.86 (m, 1H, OCH_2), 4.08–4.15 (m, 2H, OCH_2), 5.63 (dd, $J = 21.0$ Hz, $J = 9.6$ Hz, 1H, PCH), 7.40 (d, $J = 7.8$ Hz, 2H, ArH), 7.45 (d, $J = 8.4$ Hz, 2H, ArH), 8.38 (d, $J = 6.0$ Hz, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 19.75; ESI-MS: *m/z* 448 (M$^+$, 100%), 225 (51%). Anal. Calcd for $C_{15}H_{19}BrN_3O_4PS$: C 40.19, H 4.27, N 9.37; found C 39.92, H 4.10, N 9.53.

Data for **3e**: Yield 81%, colorless crystals, mp 148–149°C; IR (KBr): υ 3225 (N—H), 1666 (C=O), 1531 (C=N), 1230 (P=O), 1025 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.08 (t, $J = 6.6$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.35 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.35 (s, 3H, CH_3), 2.83 (s, 3H, CH_3), 3.62–3.65 (m, 1H, OCH_2), 3.85–3.88 (m, 1H, OCH_2), 4.11–4.18 (m, 2H, OCH_2), 5.60 (dd, $J = 20.7$ Hz, $J = 9.0$ Hz, 1H, PCH), 7.18 (d, $J = 8.4$ Hz, 2H, ArH), 7.41 (d, $J = 8.4$ Hz, 2H, ArH), 7.86 (sb, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 19.97; ESI-MS: *m/z* 405 (M$^+$+Na-1, 7%), 383 (M$^+$, 100%). Anal. Calcd for $C_{16}H_{22}N_3O_4PS$: C 50.12, H 5.78, N 10.97; found C 50.35, H 5.53, N 11.07.

Data for **3f**: Yield 75%, colorless crystals, mp 141–142°C; IR (KBr): υ 3193 (N—H), 2982 (Ar-H), 1661 (C=O), 1517 (C=N), 1246 (P=O), 1035 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.09 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.34 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.84 (s, 3H, CH_3), 3.59–3.61 (m, 1H, OCH_2), 3.79–3.83 (m, 1H, OCH_2), 4.09–4.15 (m, 2H, OCH_2), 5.62 (dd, $J = 20.7$ Hz, $J = 9.0$ Hz, 1H, PCH), 6.88 (d, $J = 8.4$ Hz, 2H, ArH), 7.46 (d, $J = 7.8$ Hz, 2H, ArH), 8.60 (sb, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 20.69; ESI-MS: *m/z* 437.9 (M^++K-1, 12%), 422 (M^++Na-1, 15%), 399.6 (M^+, 100%), 257 (14%). Anal. Calcd for $C_{16}H_{22}N_3O_5PS$: C 48.11, H 5.55, N 10.52; found C 48.39, H 5.81, N 10.66.

Data for **3g**: Yield 71%, colorless solid, mp 132–134°C; IR (KBr): υ 3226 (N—H), 2990 (Ar-H), 1667 (C=O), 1538 (C=N), 1234 (P=O), 1025 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.04 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.37 (t, $J = 7.8$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.90 (s, 3H, CH_3), 3.73–3.76 (m, 1H, OCH_2), 3.91–3.96 (m, 1H, OCH_2), 4.18–4.23 (m, 2H, OCH_2), 6.11 (dd, $J = 21.0$ Hz, $J = 9.0$ Hz, 1H, PCH), 7.25 (d, $J = 8.4$ Hz, 2H, ArH), 7.55 (d, $J = 9.0$ Hz, 2H, ArH), 7.67 (sb, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 20.81; ESI-MS: *m/z* 414.2 (M^+, 100%). Anal. Calcd for $C_{15}H_{19}N_4O_6PS$: C 43.48, H 4.62, N 13.52; found C 43.10, H 4.34, N 13.69.

Data for **3h**: Yield 82%, colorless crystals, mp 137–138°C; IR (KBr): υ 3218 (N—H), 2988 (Ar-H), 1664 (C=O), 1543 (C=N), 1236 (P=O), 1031 (P—O—C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.11 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 1.37 (t, $J = 7.2$ Hz, 3H, $CH_2C\mathbf{H_3}$), 2.87 (s, 3H, CH_3), 3.67–3.71 (m, 1H, OCH_2), 3.85–3.87 (m, 1H, OCH_2), 4.14–4.22 (m, 2H, OCH_2), 6.19 (dd, $J = 21.0$ Hz, $J = 8.4$ Hz, 1H, PCH), 7.24 (d, $J = 8.4$ Hz, 1H, ArH), 7.47 (s, 1H, ArH), 7.67 (s, 1H, ArH), 8.46 (sb, 1H, NH);^{31}P {^{1}H} NMR ($CDCl_3$, 243 MHz): δ 19.47; ESI-MS: *m/z* 437 (M^+, 100%). Anal. Calcd for $C_{15}H_{18}Cl_2N_3O_4PS$: C 41.11, H 4.14, N 9.59; found C 41.25, H 3.90, N 9.30.

Herbicidal Activity Methods

The herbicidal evaluation was carried out in the laboratory of biological activities test, Nankai University, Tianjin, China. Compounds **3** were determined with *Brassica campestris L.* and *Radix Echinochloa crus-galli* as samples of annual dicotyledonous and monocotyledonous plants, respectively, using a previously reported procedure.[15] For all of the bioassay tests, each treatment was repeated twice.

CONCLUSION

In summary, a series of novel O,O-diethyl N-{4-methyl-[1,2,3]thiadiazole-5-carbonyl}-1-amino-1-substitutedbenzyl phosphonates **3** were synthesized by the condensation of O,O-diethyl α-amino substitutedbenzyl phosphonate **1** with 4-methyl-[1,2,3]thiadiazole-5-carboxylic acid **2** under mild condition. The results of a preliminary bioassay (in vitro) indicated that some of the title compounds **3** possessed moderate to good herbicidal activities against dicotyledonous plants (*Brassica campestris L*) at the concerntration of 100 mg/L, but weaker than that of the commercially available herbicide, glyphosate, at both 100 mg/L and 10 mg/L.

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