DOI:10.1021/jf903642s

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

Synthesis and Insecticidal Evaluation of *N*-*tert*-Butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines

Jian Shang,*,† Ranfen Sun,‡ Yongqiang Li,‡ Runqiu Huang,‡ Fuchun Bi,‡ and Qingmin Wang*,‡

†Chemistry and Biologic College, Yantai University, Yantai 264005, Shandong Province, People's Republic of China and ‡State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

A series of novel *N*-*tert*-butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines were synthesized by the reaction of chlorosulfenyl(*N*-*tert*-butyl-*N*,*N*′-diacylhydrazines) with 1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine (imidacloprid) in the presence of sodium hydride. Their larvicidal activities were evaluated. All of them exhibited insecticidal activities against Oriental armyworm and bean aphids. Toxicity assays indicated that at higher concentrations (200 mg L^{-1}) the title compounds can kill aphids as fast as the parent imidacloprid in 2 h, whereas at lower concentration (10 mg L^{-1}), the title compounds can induce a premature, abnormal and lethal larval moult after 3 days of treatment, like the parent diacylhydrazines.

KEYWORDS: Synthesis; larvicidal activity; *N*-*tert*-butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines; diacylhydrazines; imidacloprid

INTRODUCTION

N-*tert*-Butyl-*N*,*N*′-diacylhydrazines as a new class of insect growth regulators have been found to mimic the action of 20-hydroxyecdysone to activate the ecdysone receptor, leading to lethal premature moulting (*1*−*3*). Among nonsteroidal ecdysone agonists, *N*-*tert*-butyl-*N*′-(4-ethylbenzoyl)-*N*-3,5-dimethylbenzoylhydrazine (RH-5992) has been the first to be commercialized as a lepidopteran-specific insecticide, with a low toxicity profile toward mammals, birds, and fishes, as well as toward nontarget arthropods such as insect pollinators, predators, and parasitoids (*4*). At present, another three new structural analogues, methloxyfenozide (RH-2485), halofenozide (RH-0345), and chromafenozide (ANS-118), have already been brought to the market (*5*, *6*). Neonicotinoids are among the most effective insecticides for the control of sucking insect pests such as aphids, whiteflies, leaf- and planthoppers, thrips, and a number of coleopteran pests. Their broad insecticidal spectra, together with good systemic properties and low mammalian toxicity, make the neonicotinoids the most rapidly expanding insecticidal class since the launch of the first compound, imidacloprid, by Bayer CropScience in 1991 (*7*, *8*).

It has been reported that biscarbamoyl sulfide derivatives of methylcarbamate insecticides retained the good insecticidal activity of the parent methylcarbamate but were substantially less toxic to the white mouse (*9*, *10*). In the previous papers from our laboratory, we described the synthesis of two series of N-sulfenylated derivatives of diacylhydrazines and found that these compounds exhibit excellent larvicidal activity (*11*, *12*). Encouraged by the reports, we developed the idea that the introduction of imidacloprid into *N*-*tert*-butyl-*N*,*N*′-diacylhydrazine would retain the good insecticidal activity of the parent imidacloprid and *N*-*tert*-butyl-*N*,*N*′-diacylhydrazine. Therefore, in a search for new insecticides with improved biological properties and different activity spectrum, we designed and synthesized a series of *N*-*tert*-butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines of the general structure **4** as shown in Scheme **2**. This article is concerned with the synthesis and biological activity of these compounds.

MATERIALS AND METHODS

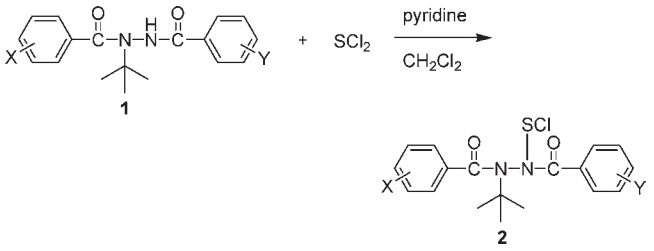
Synthetic Procedures. All reactions were carried out under a nitrogen atmosphere with the exclusion of moisture. Proton NMR spectra were obtained at 300 MHz using a Bruker AV300 spectrometer. Chemical shift values (δ) are given in ppm and are downfield from internal tetramethylsilane. Elemental analyses were determined on an MT-3 elemental analyzer. Melting points were taken on a Thomas-Hoover melting point apparatus and were uncorrected. Column chromatographic purification was carried out by using silica gel.

General Synthetic Procedure for Chlorosulfenyl(1-*tert*-butyl-1,2-diacylhydrazine) (2). To a stirred solution of sulfur dichloride (0.008 mol) and dichloromethane (15 mL) was added a solution of pyridine (0.008 mol) in dichloromethane (5 mL) dropwise at −10 °C. Then a solution of 1-*tert*-butyl-1,2-diacylhydrazine (0.007 mol) (**1**) in dichloromethane (5 mL) was added at −10 °C. The mixture was stirred at room temperature for 4 h. Then the reaction mixture was concentrated under reduced pressure and added hexane (10 mL). The mixture was filtered to give a yellow liquid. It was used for further operations without purification as shown in **Scheme 1**.

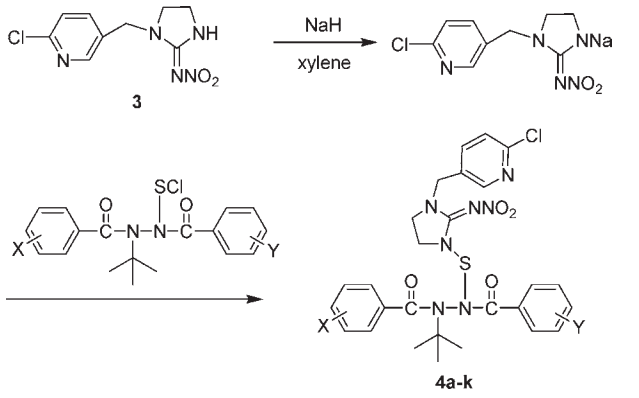
*To whom correspondence should be addressed. (J.S.) Tel: +86(0)535-6902700. Fax: +86(0)535-6902078. E-mail: shangjian.@126.com. (Q.W.) Tel: +86(0)22-23499842. Fax: +86(0)22-23499842. E-mail: wang98h@263.net; wangqm@nankai.edu.cn.

 Published on Web 12/30/2009

Scheme 1. General Synthetic Route for Chlorosulfenyl(*N*-*tert*-butyl-*N*,*N*′-diacylhydrazines) (**2**)



Scheme 2. General Synthetic Route for the Title Compounds **4a**−**4k**



General Synthetic Procedure for *N*-*tert*-Butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines (4a−k). To a stirred admixture of 1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine (imidacloprid) (0.006 mol) (**3**) in anhydrous xylene (40 mL) was added sodium hydride (0.007 mol) over a period of 5 min. The mixture was stirred at boiling temperature for 2 h and then cooled to −10 °C. Then the crude chlorosulfenyl(1-*tert*-butyl-1,2-diacylhydrazine) (**2**) solution was added dropwise. After the addition was complete, the reaction mixture was stirred for 6 h at room temperature. The solid was then filtered off, and the filtrate was concentrated under vacuum. Then the residue was purified by column chromatography on silica gel using petroleum ether (60−90 °C), dichloromethane, and ethyl acetate (20:1:1 by volume) as the eluent. *N*-*tert*-Butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines (**4a**−**k**) was obtained as shown in **Scheme 2**. The physical properties of compounds **4a**−**k** are listed in **Table 1**.

*Data for **4a***. ^{1}H NMR ($CDCl_3$, ppm): δ1.36 (br s, 9H, C(C**H**$_3$)$_3$), 3.32 (br d, 2H, C**H**$_2$), 3.71 (br s, 2H, C**H**$_2$), 4.16 (m, 1H, C**H**$_2$), 4.72 (m, 1H, C**H**$_2$), 6.64−8.14 (m, 13H, Ar**H**). Anal. Found: C, 55.78; H, 4.87; N, 16.76. Calcd. for $C_{27}H_{28}ClN_7O_4S$: C, 55.71; H, 4.85; N, 16.84.

*Data for **4b***. ^{1}H NMR($CDCl_3$): δ1.25−1.33 (m, 12H, C(C**H**$_3$)$_3$+CH$_2$-C**H**$_3$), 2.37 (s, 6H, ArC**H**$_3$), 2.71 (m, 2H, CH$_2$), 3.33 (br d, 2H, C**H**$_2$), 3.75 (br s, 2H, C**H**$_2$), 4.17 (br s, 1H, C**H**$_2$), 4.68 (br s, 1H, C**H**$_2$), 6.59−8.12 (m, 10H, Ar**H**). Anal. Found: C, 58.35; H, 5.60; N, 15.30. Calcd. for $C_{31}H_{36}ClN_7O_4S$: C, 58.34; H, 5.69; N, 15.36.

*Data for **4c***. ^{1}H NMR($CDCl_3$): δ1.35 (br s, 9H, C(C**H**$_3$)$_3$), 2.37 (s, 6H, ArC**H**$_3$), 3.32 (br d, 2H, C**H**$_2$), 3.73 (br s, 2H, C**H**$_2$), 4.17 (m, 1H, C**H**$_2$), 4.69 (m, 1H, C**H**$_2$), 6.59−8.31 (m, 11H, Ar**H**). Anal. Found: C, 57.18; H, 5.28; N, 15.93. Calcd. for $C_{29}H_{32}ClN_7O_4S$: C, 57.09; H, 5.29; N, 16.07.

*Data for **4d***. ^{1}H NMR($CDCl_3$): δ1.34 (br s, 9H, C(C**H**$_3$)$_3$), 2.35 (s, 12H, ArC**H**$_3$), 3.33 (br d, 2H, C**H**$_2$), 3.77 (br s, 2H, C**H**$_2$), 4.15 (m, 1H, C**H**$_2$), 4.70 (m, 1H, C**H**$_2$), 6.58−8.12 (m, 9H, Ar**H**). Anal. Found: C, 58.20; H, 5.80; N, 15.20. Calcd. for $C_{31}H_{36}ClN_7O_4S$: C, 58.34; H, 5.69; N, 15.36.

*Data for **4e***. ^{1}H NMR($CDCl_3$): δ1.34 (br s, 9H, C(C**H**$_3$)$_3$), 3.32 (br d, 2H, C**H**$_2$), 3.70 (br s, 2H, C**H**$_2$), 4.24 (br d, 1H, C**H**$_2$), 4.61 (br s, 1H, C**H**$_2$), 6.78−8.15 (m, 12H, Ar**H**). Anal. Found: C, 52.41; H, 4.36; N, 15.71. Calcd. for $C_{27}H_{27}Cl_2N_7O_4S$: C, 52.60; H, 4.41; N, 15.90.

*Data for **4f***. ^{1}H NMR($CDCl_3$): δ1.35 (br s, 9H, C(C**H**$_3$)$_3$), 3.33 (br d, 2H, C**H**$_2$), 3.68 (br s, 2H, C**H**$_2$), 3.86 (s, 3H, OC**H**$_3$), 4.17 (br d, 1H, C**H**$_2$), 4.70 (br d, 1H, C**H**$_2$), 6.70−8.12 (m, 12H, Ar**H**). Anal. Found: C, 54.94; H, 4.89; N, 16.11. Calcd. for $C_{28}H_{30}ClN_7O_5S$: C, 54.94; H, 4.94; N, 16.02.

*Data for **4g***. ^{1}H NMR($CDCl_3$): δ1.37 (br s, 9H, C(C**H**$_3$)$_3$), 3.35 (br d, 2H, C**H**$_2$), 3.82 (br s, 2H, C**H**$_2$), 4.14 (br d, 1H, C**H**$_2$), 4.72 (br s, 1H, C**H**$_2$), 6.59−8.10 (m, 12H, Ar**H**). Anal. Found: C, 52.72; H, 4.39; N, 16.05. Calcd. for $C_{27}H_{27}Cl_2N_7O_4S$: C, 52.60; H, 4.41; N, 15.90.

*Data for **4h***. ^{1}H NMR($CDCl_3$): δ1.35 (br s, 9H, C(C**H**$_3$)$_3$), 3.36 (br d, 2H, C**H**$_2$), 3.70 (br s, 2H, C**H**$_2$), 4.22 (br d, 1H, C**H**$_2$), 4.63 (br s, 1H, C**H**$_2$), 6.77−8.15 (m, 12H, Ar**H**). Anal. Found: C, 52.78; H, 4.67; N, 15.68. Calcd. for $C_{27}H_{27}Cl_2N_7O_4S$: C, 52.60; H, 4.41; N, 15.90.

*Data for **4i***. ^{1}H NMR($CDCl_3$): δ1.35 (br s, 9H, C(C**H**$_3$)$_3$), 3.35 (br d, 2H, C**H**$_2$), 3.80 (br s, 2H, C**H**$_2$), 3.94 (s, 3H, OC**H**$_3$), 4.07 (br d, 1H, C**H**$_2$), 4.79 (br d, 1H, C**H**$_2$), 6.45−8.17 (m, 12H, Ar**H**). Anal. Found: C, 54.92; H, 4.90; N, 15.95. Calcd. for $C_{28}H_{30}ClN_7O_5S$: C, 54.94; H, 4.94; N, 16.02.

*Data for **4j***. ^{1}H NMR($CDCl_3$): δ1.34 (br s, 9H, C(C**H**$_3$)$_3$), 3.27 (br d, 2H, C**H**$_2$), 3.81 (br s, 2H, C**H**$_2$), 3.88 (s, 3H, OC**H**$_3$), 3.92 (s, 3H, OC**H**$_3$), 4.18 (br d, 1H, C**H**$_2$), 4.74 (br d, 1H, C**H**$_2$), 6.59−8.19 (m, 11H, Ar**H**). Anal. Found: C, 54.16; H, 5.29; N, 15.38. Calcd. for $C_{29}H_{32}ClN_7O_6S$: C, 54.24; H, 5.02; N, 15.27.

*Data for **4k***. ^{1}H NMR($CDCl_3$): δ1.31 (br s, 9H, C(C**H**$_3$)$_3$), 3.35 (br d, 2H, C**H**$_2$), 3.68 (br s, 2H, C**H**$_2$), 3.86 (s, 6H, OC**H**$_3$), 4.13 (m, 1H, C**H**$_2$), 4.69 (m, 1H, C**H**$_2$), 6.69−8.11 (m, 11H, Ar**H**). Anal. Found: C, 54.12; H, 4.96; N, 15.28. Calcd. for $C_{29}H_{32}ClN_7O_6S$: C, 54.24; H, 5.02; N, 15.27.

Table 1. Physical Properties of Compounds **4a**−**k**

compd	X	Y	mp (°C)	yield (%)	states
4a	H	H	163−165	31.5	colorless crystal
4b	3,5-Me$_2$	4-Et	173−175	60.5	colorless crystal
4c	3,5-Me$_2$	H		11.7	colorless semisolid
4d	3,5-Me$_2$	3,5-Me$_2$		10.0	colorless semisolid
4e	4-Cl	H	177−179	62.2	colorless crystal
4f	4-OMe	H	180−182	38.1	colorless crystal
4g	2-Cl	H		22.2	colorless semisolid
4h	3-Cl	H	175−177	23.0	colorless crystal
4i	2-OMe	H	187−189	38.1	colorless crystal
4j	2-OMe	2-OMe	198−120	46.8	colorless crystal
4k	4-OMe	4-OMe	125−127	57.1	colorless crystal

Table 2. Larvicidal Activities of Products **4a**−**k** and Their Parent Compounds **1a**−**k** and **3** against Oriental Armyworm[a]

	larvicidal activities (mg L^{-1})						
compd	500	200	100	50	25	10	5
4a	100	80	0				
1a				100	70	0	
4b				100	100	90	70
1b						100	70
4c	95	85	55	10	0		
1c				100	60	10	
4d	100	70	50	25	10	0	
1d				95	70	10	
4e	100	80	70	40	0		
1e				100	100	25	0
4f	80	70	20	0			
1f	60	0					
4g	100	60	50	30	10	0	
1g				100	90	75	0
4h	100	80	70	25	0		
1h			100	95	45	0	
4i	90	40	20	0			
1i				100	90	10	0
4j	80	70	40	10	0		
1j	10	0					
4k	100	70	40	0			
1k	95	40	10	0			
3		100	60	30	20	10	

[a] **1a**, RH-5849; **1b**, RH-5992; **3**, imidacloprid.

Biological Assay. *Insecticidal Activity against Oriental Armyworm* (*Mythimna separata*). The larvicidal activities of the title compounds (**4a**−**k**) against the Oriental armyworm were evaluated and compared with those of the parent compounds **1a**−**k** and **3** using a previously reported procedure (*13*, *14*). The larvicidal activity was tested against the Oriental armyworm [*Mythimna* (= *Pseudaletia*) *separata* (Walker)] by foliar application. For the foliar armyworm tests, individual corn leaves were placed on moistened pieces of filter paper in Petri dishes. The leaves were then sprayed with the test solution and allowed to dry. The dishes were infested with 10 fourth-instar armyworm larvae. Percentage mortalities were evaluated after 4 days of treatment. Evaluations are based on a percentage scale of 0−100 in which 0 = no activity and 100 = total killed. The larvicidal activity is summarized in **Table 2**.

Insecticidal Activity against Bean Aphids (*Aphis fabae Scopoli*). The insecticidal activities of the title compound (**4a**−**k**), the parent compounds **1a**−**k**, and **3** against bean aphids were evaluated using a previously reported procedure (*15*). Bean aphids were dipped according to a slightly modified FAO dip test. The tender shoots of soybean with 40−60 healthy apterous adult aphids were dipped in the diluted solutions of the compounds for 5 s and the superfluous fluid removed and placed in a conditioned room. Mortality was calculated 48 h after treatment. Each treatment was performed three times. The revised death rate was calculated by the Abbott formula. The insecticidal activity is summarized in **Table 3**.

RESULTS AND DISCUSSION

Synthesis. The title compounds were prepared by the reaction of chlorosulfenyl(1-*tert*-butyl-1,2-diacylhydrazine) (**2**) with 1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine (imidacloprid) (**3**) in the presence of sodium hydride as shown in **Scheme 2**. Chlorosulfenyl(1-*tert*-butyl-1,2-diacylhydrazine) (**2**) was prepared in excellent yields by the reaction of sulfur dichloride with 1-*tert*-butyl-1,2-diacylhydrazine (**1**) in dichloromethane using pyridine as the acid acceptor as shown in **Scheme 1**. Chlorosulfenyl(1-*tert*-butyl-1,2-diacylhydrazine) (**2**) without further purification was reacted with 1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine (imidacloprid) (**3**) to give products **4**.

Table 3. Insecticidal Activities against Bean Aphids (200 mg L^{-1})[a]

compd	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j	4k
death rate %	100	53	80	89	87	95	84	86	92	91	87
compd	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**
death rate%	0	0	12	10	26	0	18	12	32	0	22

[a] The death rate of imidacloprid is 100% at 200 mg L^{-1}.

Structure. As the ^{1}H NMR of **4** cannot be used to verify N−CH_2−, they generally have bread or multiple formants. We determined its structure using the X-ray crystallography data. The results demonstrate that compound **4g** has the desired structure despite the fact that the ^{1}H NMR not having the ordinary formant of N−CH_2−. The molecular structure of compound **4g** was reported (*16*) as shown in **Figure 1**.

Bioassay. We combined the bioactive units of diacylhydrazine (**1**) and imidacloprid (**3**) to design and synthesize novel compounds **4a**−**k**. The results of insecticidal activities given in **Tables 2** and **3** showed that the title compounds **4a**−**k** exhibit insecticidal activities against the Oriental armyworm and bean aphids. Compound **4b** exhibited 90% larvicidal activity at 10 mg L^{-1}, which is parallel to its corresponding parent **1b** (RH-5992). Compounds **4f** and **4j** displayed higher larvicidal activities against the Oriental armyworm than their corresponding parents **1f** and **1j**, which suggested that introduction of imidacloprid into *N*-*tert*-butyl-*N*,*N*′-diacylhydrazine through nirogen−sulfur−nitrogen bond formation had a positive effect on larvicidal activities.

These derivatives have increased dissolvability relative to the parents **1** and are soluble in most organic solvents. The mode of action of the title compounds **4a**−**k** is very interesting. Toxicity assays indicated that at higher concentrations (200 mg L^{-1}) the title compounds can kill aphids as fast as the parent compounds **3** in 2 h, whereas at lower concentration (10 mg L^{-1}), the title compounds can induce a premature, abnormal, and lethal larval moult after 3 days of treatment, like the parent compounds **1**.

In summary, a series of novel *N*-*tert*-butyl-*N*′-thio[1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine]-*N*,*N*′-diacylhydrazines were synthesized by the reaction of chlorosulfenyl(*N*-*tert*-butyl-*N*,*N*′-diacylhydrazines) with imidacloprid in the presence of sodium hydride. These derivatives have increased dissolvability relative to the parents **1** and are soluble in most organic

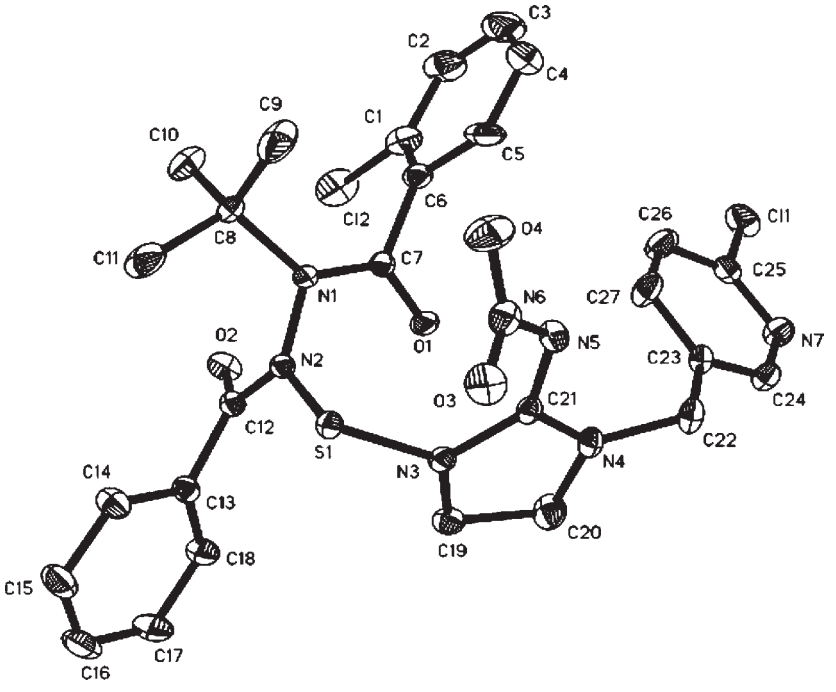


Figure 1. Molecular structure of the title compound **4g**.

solvents. All of them exhibited insecticidal activities against the Oriental armyworm and bean aphids. Interestingly, toxicity assays indicated that these products have both insecticidal activities as fast as imidacloprid at higher concentration and insect growth regulators' activities like those of diacylhydrazines at lower concentrations. The results are promising, and further studies on insecticidal activities and systemic activities of the title compounds are underway and will be reported in due course.

LITERATURE CITED

(1) Wing, K. D. RH5849, a nonsteroidal ecdysone agonist: Effects on a *Drosophila* cell line. *Science* **1988**, *241*, 467–469.

(2) Wing, K. D.; Slawecki, R. A.; Carlson, G. R. RH5849, a nonsteroidal ecdysone agonist: Effects on larval Lepidoptera. *Science* **1988**, *241*, 470–472.

(3) Wing, K. D. Anthelmintic N′-substituted-N,N′-disubstituted-hydrazines. U.S. Patent 5,424,333, 1995.

(4) Dhadialla, T. S.; Jansson, R. K. Non-steroldal ecdysone agonists: New tools for IPM and insect resistance management. *Pestic. Sci.* **1999**, *55*, 357–359.

(5) Carlson, G. R.; Dhadialla, T. S.; Hunter, R. The chemical and biological properties of methoxyfenozide, a new insecticidal ecdysteroid agonist. *Pest Mang. Sci.* **2001**, *57*, 115–119.

(6) Hsu, A. C. T. 1,2-Diacyl-1-alkylhydrazines, a New Class of Insect Growth Regulators. In *Synthesis and Chemistry of Agrochemical II*; Baker, B. R., Fenyes, J. G., Moberg, W. K., Eds.; ACS Symposium Series 443, American Chemical Society: Washington, DC, 1991; pp 478−490.

(7) Elbert, A.; Hass, M.; Springer, B.; Thielert, W.; Nauen, R. Applied aspects of neonicotinoid uses in crop protection. *Pest Manag. Sci.* **2008**, *64*, 1099–1105.

(8) Shao, X. S; Li, Z.; Qian, X. H.; Xu, X. Y. Design, synthesis, and insecticidal activities of novel analogues of neonicotinoids: replacement of nitromethylene with nitroconjugated system. *J. Agric. Food Chem.* **2009**, *57*, 951–957.

(9) Drabek, J. Bis-(O-1-alkylthio-ethylimino)-N-methyl-carbamic acid)-N,N′-sulphide insecticides. U.S. Patent 4,004,031, 1977.

(10) Fahmy, M. A. H.; Chiu, Y. C.; Fukuto, T. R. Selective toxicity of N-substituted biscarbamoyl sulfides. *J. Agric. Food Chem.* **1974**, *22*, 59–62.

(11) Wang, Q. M.; Huang, R. Q.; Bi, F. C.; Li, Z. G. Synthesis and biological activity of novel N-sulfenylated derivatives of diacylhydrazines. *J. Chem. Res.* **2001**, 342–343.

(12) Wang, Q. M.; Cheng, J. R.; Huang, R. Q. Synthesis and insecticidal evaluation of novel N-(S-amino)sulfenylated derivatives of diacylhydrazines. *Pest Manag. Sci.* **2002**, *58*, 1250–1253.

(13) Hsu, A. C.; Aller, H. E. Insecticidal N′-substituted-N,N′-disubstituted-hydrazines. U.S. Patent 5,117,057, 1993.

(14) Mao, C. H.; Wang, Q. M.; Huang, R. Q.; Bi, F. C.; Chen, L.; Liu, Y. X.; Shang, J. Synthesis and insecticidal evaluation of novel N-oxalyl derivatives of Tebufenozide. *J. Agric. Food Chem.* **2004**, *52*, 6737–6741.

(15) Zhao, Y.; Li, Y. Q.; Ou, X. M.; Zhang, P. X.; Wang, Q. M. Synthesis, insecticidal, and acaricidal activities of novel 2-aryl-pyrrole derivatives containing ester groups. *J. Agric. Food Chem.* **2008**, *56*, 10176–10182.

(16) Shang, J.; Wang, Q. M.; Huang, R. Q.; Chen, L.; Gao, J. H. N′-Benzoyl-N-tert-butyl-2-chloro-N′-{[3-(6-chloro-3-pyridylmethyl)-2-nitriminoimidazolidin-1-yl]sulfanyl}-benzohydrazide. *Acta Crystallogr., Sect. E* **2009**, *65*, o2131–o2132.

Received for review October 17, 2009. Revised manuscript received December 16, 2009. Accepted December 17, 2009. We gratefully acknowledge the support of this work by the National Key Project for Basic Research (2010CB126106) and the National Natural Science Foundation of China (20672064).