J. Pesticide Sci. **19**, 119–125 (1994)

Original Article

Synthesis and Insecticidal Activity of Acyclic Nitroethene Compounds Containing (6-Substituted)-3-pyridylamino Group*

Takanori TABUCHI, Takafumi FUSAKA, Koichi IWANAGA,**
Isao MINAMIDA and Tetsuo OKAUCHI

Agricultural Research Laboratories, Agro Division, Takeda Chemical Industries, Ltd., Wadai, Tsukuba 300–42, Japan
***Animal Health Research Laboratories, Agro Division, Takeda Chemical Industries, Ltd., Yodogawa-ku, Osaka 532, Japan*

(Received September 24, 1993; Accepted January 7, 1994)

Modification of 1-methylamino-1-[*N*-methyl-*N*-(3-pyridylmethyl)]amino-2-nitroethene (**1**) was progressed stepwise with reference to the insecticidal activities of compounds prepared so far against *Nilaparvata lugens*. Firstly, we replaced the methylene of **1** with a chemical bond (**3**), an ethylidene (**4**) or an ethylene (**5**), and found that the activity of 1-methylamino-1-[*N*-methyl-*N*-(3-pyridyl)]amino-2-nitroethene (**3**) was higher than others and comparable to **1**. Secondly, introduction of a methyl (**6**), a methoxy (**7**) or a chloro group (**8**) into the 6-position of the pyridine of **3** afforded 1-[*N*-(6-chloro-3-pyridyl)-*N*-methyl]amino-1-methylamino-2-nitroethene (**8**) as the best among the compounds derived. Finally, substitution of either one or both of the methyl groups of **8** with a hydrogen or higher alkyls (**9–15**) or formylation of **8** gave rise to 1-[*N*-(6-chloro-3-pyridyl)-*N*-methyl]amino-1-(*N*-formyl-*N*-methyl)amino-2-nitroethene (**17**) as the top of the derivatives which exhibited potent activity against not only *N. lugens* but also *Spodoptera litura*.

INTRODUCTION

In our preceding report,[1] derivatives of nitroethene having a 3-pyridylmethylamino and an alkylamino group at the β-position were synthesized and shown to be potently active against hemipterous insects such as *Nilaparvata lugens*, *Laodelphax striatellus* and *Nephotettix cincticeps*. Among them, 1-methylamino-1-[*N*-methyl-*N*-(3-pyridylmethyl)]amino-2-nitroethene (**1**) was chosen as a key compound for the most potent activity. The subsequent modification of **1** in our second report[2] has yielded nitenpyram (**2**) which is exceedingly active against the hemipterous insects and now on extended evaluations.

For further modification, first we replaced the methylene of **1** with another joint residue as a single bond (**3**), an ethylidene (**4**) and an ethylene (**5**). Then we progressed the modification stepwise by choosing the most potent, **3** in the present step, in reference with the activities of the compounds prepared so far against *N. lugens* and by putting it into the next step modification.

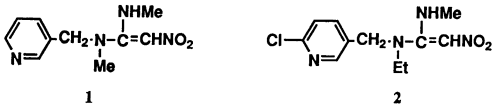
This report deals with the three step modification of **1** leading to 1-[*N*-(6-chloro-3-pyridyl)-*N*-methyl]amino-1-(*N*-formyl-*N*-methyl)amino-2-nitroethene (**17**) which is active against not only *N. lugens* but also *Spodoptera litura*.

MATERIALS AND METHODS

1. *Synthesis of Compounds*

Several aminopyridines used were prepared

* Studies on Acyclic Nitroethene Compounds (Part 3). For Part 2, see Ref. 2).



1 2

Fig. 1 A key compound (**1**) and nitenpyram (**2**) described in the preceding paper.[1,2]

by conventional methods.[3-6]

All of the compounds except **9**, **16** and **17** in Tables 1, 2 and 3 were prepared by Method A. Compounds **9**, **16** and **17** were prepared by Methods B, C and D respectively (Fig. 2).

General synthetic procedure is described in previous paper.[1]

Typical examples of synthetic procedures are as follows.

1.1 Method A

1-[N-(6-Chloro-3-pyridyl)-N-methyl]amino-1-methylamino-2-nitroethene (**8**)

In 50 ml of acetonitrile, 4.0 g (0.028 mol) of 2-chloro-5-methylaminopyridine and 3.7 g of methyl isothiocyanate were refluxed for 52.5 hr and the reaction mixture was concentrated. To the residue were added 30 ml of ice-water containing 2 ml of 3 N HCl, followed by extraction with AcOEt (50 ml×3). The extracts were pooled, washed successively with 3 N HCl (4 times), aqueous sodium chloride solution (4 times) and aqueous sodium hydrogen carbonate solution (once), and dried over $MgSO_4$. The solvent was distilled off under reduced pressure, and after addition of ether, the crystals were collected by filtration and dried to give 2.8 g (46%) of 1,3-dimethyl-1-(6-chloro-3-pyridyl)thiourea as white crystals. mp 87.5–88°C. Anal. Found: C, 44.53; H, 4.68; N, 19.28, Calcd. for $C_8H_{10}N_3SCl$: C, 44.55; H, 4.67; N, 19.48%. IR ν_{max}^{Nujol} cm^{-1}: 3280, 1525. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 3.09 (3H, d, J=4.5 Hz), 3.65 (3H, s), 5.3–6.0 (1H, m), 7.47 (1H, d, J=8.4 Hz), 7.61 (1H, dd, J=8.4 and 2.4 Hz), 8.33 (1H, d, J=2.4 Hz).

In 10 ml of dry tetrahydrofuran was suspended 0.9 g of 60% sodium hydride (in oil) which had been washed twice with petroleum ether, and with stirring, a solution of 2.5 g (0.012 mol) of 1,3-dimethyl-1-(6-chloro-3-pyridyl)thiourea in 30 ml of dry tetrahydrofuran was added dropwise. After completion of addition, the mixture was stirred at 50°C for 0.5 hr. Then, at room temperature, 2.2 g of methyl iodide was added dropwise and the mixture was further stirred for 3 hr. The reaction mixture was concentrated under reduced pressure, and after addition of 50 ml of iced water containing 3 ml of 3 N HCl, the concentrate was extracted with AcOEt (50 ml×

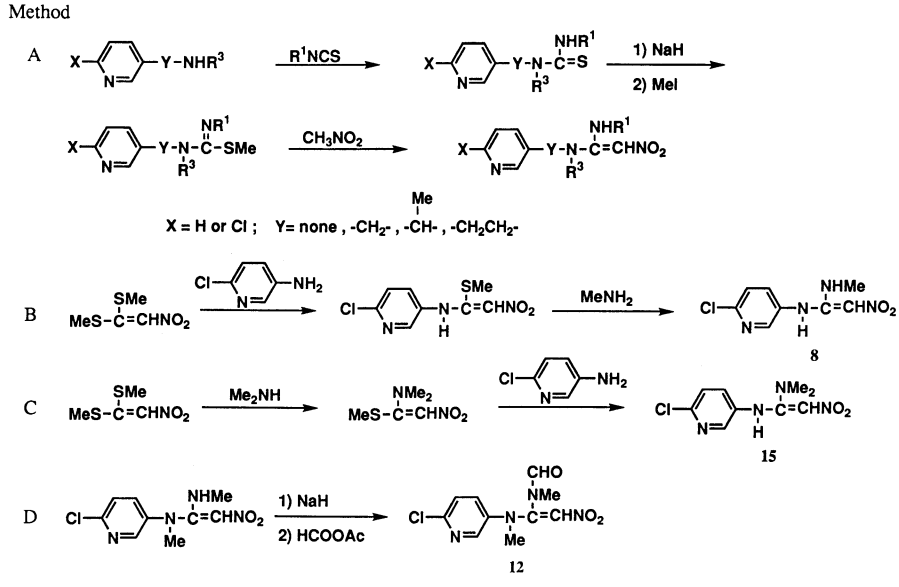


Fig. 2 Syntheses of acyclic nitroethene compounds.

3). The extracts were pooled, washed with water (twice) and dried over $MgSO_4$. Finally, the solvent was distilled off under reduced pressure to give 2.6 g of crude *E* and *Z* mixture of *S*,1,3-trimethyl-3-(6-chloro-3-pyridyl)isothiourea as a brown oil. IR ν_{max}^{Neat} cm^{-1}: 1615. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 2.07 (1.5H, s), 2.38 (1.5H, s), 3.06 (1.5H, s), 3.27 (1.5H, s), 3.17 (1.5H, s), 3.30 (1.5H, s), 6.90–7.60 (2H, m), 7.90 (0.5H, d, J=3.0 Hz), 8.24 (0.5H, d, J=3.0 Hz).

To crude *S*,1,3-trimethyl-3-(6-chloro-3-pyridyl)isothiourea (2.60 g) was added 40 ml of nitromethane and the mixture was refluxed for 63 hr. The reaction mixture was concentrated and the residue was subjected to silica gel column chromatography using hexane–acetone (1 : 2) as an eluent to give 1.30 g (47%) of the title compound as pale yellow crystals. mp 108–109°C. Anal. Found: C, 44.50; H, 4.72; N, 23.21, Calcd. for $C_9H_{11}N_4O_2Cl$: C, 44.55; H, 4.57; N, 23.09%. IR ν_{max}^{Nujol} cm^{-1}: 3120, 1600. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 2.75 (3H, d, J=5.1 Hz), 3.30 (3H, s), 6.63 (1H, s), 7.2–7.6 (2H, m), 8.2–8.3 (1H, m), 9.6–10.3 (1H, m).

1.2 Method B

1-(6-Chloro-3-pyridyl)amino-1-methylamino-2-nitroethene (**9**)

A mixture of 3.9 g (0.0303 mol) of 5-amino-2-chloropyridine, 5.0 g of 1,1-bis(methylthio)-2-nitroethene and 80 ml of ethylbenzene was heated at 130°C for 2 hr. Ethylbenzene was distilled off under reduced pressure and the crystalline residue was washed with AcOEt and subjected to silica gel column chromatography using EtOH–$CHCl_3$ (1 : 30) as the eluent to recover crude crystals. These crystals were recrystallized from AcOEt, washed with ether and dried. The procedure gave 0.5 g of 1-(6-chloro-3-pyridyl)amino-1-methylthio-2-nitroethene as pale yellow crystals. mp 169–171°C. Anal. Found: C, 39.06; H, 3.25; N, 17.21, Calcd. for $C_8H_8N_3O_2SCl$: C, 39.11; H, 3.28; N, 17.10%. IR ν_{max}^{Nujol} cm^{-1}: 3100, 1575, 1175. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 2.42 (3H, s), 6.70 (1H, s), 7.41 (1H, dd, J=9.0 Hz), 7.65 (1H, dd, J=9.0 and 2.4 Hz), 8.41 (1H, d, J=2.4 Hz), 11.3–11.8 (1H, br).

In 25 ml of EtOH was dissolved 0.42 g (0.00171 mol) of 1-(6-chloro-3-pyridyl)amino-1-methylthio-2-nitroethene, followed by addition of 0.2 g of a 40% solution of methylamine in methanol. The mixture was refluxed for 1.5 hr. The solvent was distilled off and the crystalline residue was washed with AcOEt and dried to give 0.33 g of the title compound as white crystals. mp 185°C (decomp.). Anal. Found: C, 41.98; H, 4.01; N, 24.62, Calcd. for $C_8H_9N_4O_2Cl$: C, 42.03; H, 3.97; N, 24.50%. IR ν_{max}^{Nujol} cm^{-1}: 3150, 1635, 1210. ^1H NMR $\delta_{TMS}^{DMSO\text{-}d_6}$ ppm: 2.94 (3H, d, J=5.4 Hz), 6.24 (1H, s), 7.57 (1H, d, J=9.0 Hz), 7.80 (1H, dd, J=9.0 and 2.7 Hz), 8.34 (1H, d, J=2.7 Hz), 8.8–9.7 (1H, br), 9.2–10.3 (1H, br).

1.3 Method C

1-(6-Chloro-3-pyridyl)amino-1-dimethylamino-2-nitroethene (**16**)

In 50 ml of EtOH was dissolved, 1,1-bis-(methylthio)-2-nitroethene (3.30 g) under heating, and 50% aqueous solution of dimethylamine(2.20 ml) was added dropwise in two portions at 30 min intervals under reflux. After refluxed for 30 min, the solvent was distilled off, and the residue was chromatographed on a silica gel column with AcOEt to give 1.00 g (31%) of 1-dimethylamino-1-methylthio-2-nitroethene as a yellow oil. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 2.46 (3H, s), 3.21 (6H, s), 6.69 (1H, s).

A mixture of 1.5 g (0.0093 mol) of 1-dimethylamino-1-methylthio-2-nitroethene and 1.1 g of 5-amino-2-chloropyridine was heated at 110–120°C with stirring for 1 hr. After cooling, the reaction mixture was subjected to silica gel column chromatography using EtOH–$CHCl_3$ (1 : 40) as the eluent to give 0.38 g of the title compound as pale brown crystals. The NMR spectrum of this product showed that it was a 1 : 1 mixture of the title compound and N^2-(6-chloro-3-pyridyl)-N^1, N^1-dimethyl-2-nitroacetamidine. mp 122–123°C. Anal. Found: C, 44.64; H, 4.57; N, 23.03, Calcd. for $C_9H_{11}N_4O_2Cl$: C, 44.55; H, 4.57; N, 23.09%. IR ν_{max}^{Nujol} cm^{-1}: 3100, 1395, 1280. ^1H NMR $\delta_{TMS}^{DMSO\text{-}d_6}$ ppm: 2.86 (3H, s), 3.10 (3H, s), 5.17 (1H, s), 6.68 (0.5H, s), 7.09 (0.5H, dd, J=9.0 and 2.7 Hz), 7.24 (0.5H, d, J=9.0 Hz), 7.3–7.6 (1H, m), 7.86 (0.5H, d, J=2.7 Hz), 8.22 (0.5H, d, J=2.7 Hz), 10.8–11.2 (0.5H, br).

1.4 Method D

1-[N-(6-Chloro-3-pyridyl)-N-methyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethene (**17**)

To a suspension of 60% sodium hydride in)

oil: 0.10 g) in 10 ml of dry THF was added a solution of 1-[*N*-(6-chloro-3-pyridyl)-*N*-methyl]amino-1-methylamino-2-nitroethene (0.68 g) in 5 ml of dry THF and stirred at room temperature for 1 hr. Formic acetic anhydride (0.70 g) was then added dropwise to the solution at 0°C and stirred for 3 hr. The solvent was distilled off under reduced pressure and the residue was diluted with CH_2Cl_2 and washed with brine. After dried over $MgSO_4$ and concentrated, the residue was subjected to purification by silica gel column chromatography using hexane–acetone (1: 1) as an eluent to give 0.16 g (24%) of the title compound as yellow crystals. mp 134–135°C. Anal. Found: C, 44.25; H, 4.08; N, 20.58, Calcd. for $C_{10}H_{11}N_4O_3Cl$: C, 44.37; H, 4.10; N, 20.70%. IR ν_{max}^{Nujol} cm^{-1}: 1685, 1560, 1305, 1280, 1250, 1135. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 2.73 (1.5H, s), 2.89 (1.5H, s), 3.32 (1.5H, s), 3.39 (1.5H, s), 7.03 (0.5H, s), 7.10 (0.5H, s), 7.46 (0.5H, d, J=8.0 Hz), 7.57 (0.5H, d, J=8.0 Hz), 7.83 (0.5H, dd, J=8.0 and 2.0 Hz), 7.92 (0.5H, dd, J=8.0 and 2.0 Hz), 8.35 (0.5H, s), 8.37 (0.5H, d, J=2.0 Hz), 8.44 (0.5H, d, J=2.0 Hz), 8.70 (0.5H, s).

2. Biological Tests

2.1 Against N. lugens

Each test compound was sprayed at the indicated concentrations over stems and leaves of rice seedlings in the 2-leaf stage at a rate of 10 ml per paper pot. Water was put in test tubes, and the treated rice seedlings were placed therein. Then 10 (or 20) 3rd-instar larvae of *N. lugens* were released in each tube, which was then capped with an aluminum cap. The test tubes were maintained in an incubator at 25°C, and dead insects were counted 7 days after release. The % mortality was calculated using the following formula.

$$\text{Mortality (\%)} = (\text{Number of dead insects}/\text{Number of insects released}) \times 100$$

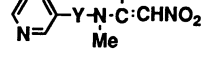
2.2 Against S. litura

A solution of a test compound at the indicated concentrations was applied to soybean seedlings at the simple leaf unfolding stage at a rate of 20 ml per pot by a spray gun. After the applied chemical solution had been dried, two simple leaves per seedling were shorn off and placed in a plastic cup to which 10 (or 20) third-instar larvae of *S. litura* were released. After release, the cup was placed in an incubator at 25°C. The number of dead insects was counted 5 days after release. The mortality rate was calculated by means of the equation given in *2.1*.

RESULTS AND DISCUSSION

Table 1 shows the effect of replacement of the methylene of the key compound (**1**) with

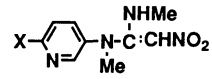
Table 1 Insecticidal activity against *N. lugens* and *N. cincticeps* of acyclic nitroethene compounds.



Compd. No.	Y	mp (°C)	Yield[a] (%)	Mortality (%)				
				N. lugens			*N. cincticeps*	
				500	200	40	200	40 (ppm)
1	$-CH_2-$	86–87	28	100	100	100	100	100
3	—	113–114	55	100	100	100	85	30
4	–CHMe–	oil[b]	60	100	100	80	100	85
5	$-CH_2CH_2-$	oil[c]	100	100	10	10	10	5
Comparative compound (propaphos)				100	90	40	100	95

[a] Based on the corresponding isothiourea. [b] ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 1.70 (3H, d), 2.63 (3H, s), 3.02 (3H, d), 4.93 (1H, q), 6.50 (1H, s), 7.33 (1H, dd), 7.60 (1H, m), 8.60 (2H, m), 9.77 (1H, br). [c] ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 2.93 (3H, d), 2.96 (3H, s), 2.97 (2H, m), 3.50 (2H, m), 6.52 (1H, s), 7.27 (1H, dd), 7.57 (1H, m), 8.50 (2H, m), 9.67 (1H, br).

Table 2 Insecticidal activity against *N. lugens* and *S. litura* of 1-methylamino-1-[*N*-methyl-*N*-(6-substituted)-3-pyridyl]amino-2-nitroethenes.



Compd. No.	X	mp (°C)	Yield[a] (%)	Mortality (%)						
				N. lugens				*S. litura*		
				500	200	40	2.5	500	100	20 (ppm)
3	H	113–114	55	100	100	—	80	10	—	—
6	6-Me	120–121	64	100	100	95	30	100	20	10
7	6-OMe	131–132	71	100	—[b]	—	20	100	60	25
8	6-Cl	108–109	47	100	100	90	70	100	100	55
Comparative compounds[c]				100	90	40	—	100	100	10

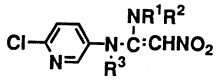
[a] Based on the corresponding isothiourea. [b] Not tested. [c] Propaphos and acephate were used against *N. lugens* and *S. litura* respectively.

a chemical bond (**3**), an ethylidene (**4**) and an ethylene (**5**) on insecticidal activity. Against *N. lugens*, desmethylene congener (**3**) was comparable to **1**, whereas ethylidene congener (**4**) was slightly inferior to **1**, and ethylene congener (**5**) was the least active among them. Such comparableness of **3** to **1** was lost and **3** turned out to be inferior to **1** when they were applied against *N. cincticeps*. Thus, the activity order of the derivatives was **1**>**3**>**4**>**5**. It is interesting to compare above results with those reported for the replacement of the methylene of *N*-(6-chloro-3-pyridylmethyl)-2-nitromethylene imidazolidine with a chemical bond and an ethylene by Tomizawa & Yamamoto.[7] They reported that activities against *N. cincticeps* were in the order of methylene> desmethylene>ethylene congeners. Given our experiences that *N. lugens* and *N. cincticeps* showed a similar trend of sensitivities, with a difference in degree, to nitromethylene derivatives,[1,2] it can be stated that both series of acyclic nitroethenes as **1**, **3**, **5** and cyclic nitromethylenes as cited above showed similar structure-activity relationships due to attacking the same binding site, *i.e.*, nicotinoid-receptor, of target insects.

We were interested in the relatively high insecticidal activities of desmethylene congener (**3**), and hence challenged to modify **3** in order to find more active and/or broader spectrum compounds. As the following step, we introduced substituents to the pyridyl part of **3**, and the results are listed in Table 2. Against *N. lugens*, unsubstituted pyridyl (**3**) and chloro (**8**) derivatives showed more than 70% mortality at 2.5 ppm, but the activities of others were reduced at the same concentration. While against *S. litura*, methyl (**6**), methoxy (**7**) and chloro (**8**) derivatives showed 100% mortality at 500 ppm. It is worth noting that compound **8** showed 100% mortality at 100 ppm and was superior against *S. litura* to 1-[*N*-(6-chloro-3-pyridylmethyl)-*N*-ethyl]amino-1-methylamino-2-nitroethene (nitenpyram: **2**), the activity of which was not strong enough against lepidpterous insects for practical use (The mortality against *S. litura* was 80% at 500 ppm). The activity against *S. litura* encouraged us to prepare and test further compounds carrying 6-chloro-3-pyridylamino group.

As the next step, we attempted to modify the three substituents R^1, R^2 and R^3 on nitrogen atoms and the results are shown in Table 3. When R^1R^2N was methylamino group, compounds whose R^3 was ethyl (**10**) or *n*-propyl (**13**) showed 100% mortality against *N. lugens* at 2.5 ppm. In the case of smaller (H, **9**; Me, **8**) or larger (*n*-Bu, **15**) substituents, the activities decreased. Compound **16** whose R^1R^2N was dimethylamino group showed high insecticidal activity even though R^3 was hydrogen atom. When R^3 was methyl group, compounds whose R^1R^2N was ethylamino (**11**) or *N*-formyl-*N*-methylamino (**17**) group show-

Table 3 Insecticidal activity against *N. lugens* and *S. litura* of 1-[*N*-(6-chloro-3-pyridyl)-*N*-(substituted)amino]-1-substituted amino-2-nitroethenes.



Compd. No.	R^1	R^2	R^3	mp (°C)	Yield[a] (%)	Mortality (%)							
						N. lugens					*S. litura*		
						500	200	40	2.5	0.5	500	100	20(ppm)
9	Me	H	H	185 (dec.)	84	100	—[b]	—	50	10	100	30	35
8	Me	H	Me	108–109	47	100	100	90	70	10	100	100	55
10	Me	H	Et	95–96	23	100	—	—	100	40	60	—	—
11	Et	H	Me	118–119	36	100	—	—	100	40	60	—	—
12	Et	H	Et	105–106	29	100	75	25	20	10	10	—	—
13	Me	H	^{n}Pr	95–95	31	100	—	—	100	50	10	—	—
14	^{n}Pr	H	Me	Oil[c]	32	100	35	15	10	5	20	—	—
15	Me	H	^{n}Bu	87–88	35	100	—	—	10	10	10	—	—
16[d]	Me	Me	H	122–123	18	100	—	—	90	50	80	—	—
17	Me	CHO	Me	134–135	24	100	—	—	100	50	100	100	40

[a] Based on the corresponding isothiourea except for **9**, **16** and **17**. [b] Not tested. [c] ^{1}H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 0.93 (3H, t, J=7.2 Hz), 1.59 (2H, tq, J=7.2 and 7.2 Hz), 2.95 (2H, dt, J=6.0 and 7.2 Hz), 3.30 (3H, s), 6.60 (1H, s), 7.2–7.6 (2H, m), 8.23 (1H, d, J=3.0 Hz), 9.6–10.1 (1H, br). [d] Existed as an isomeric mixture of 1-(6-chloro-3-pyridyl)amino-1-dimethylamino-2-nitroethene and N^2-(6-chloro-3-pyridyl)-N^1, N^1-dimethyl-2-nitroacetamidine in $CDCl_3$.

ed 100% mortality at 2.5 ppm. Smaller (Me, **8**) or larger (*n*-Pr, **14**) substituent gave reduced insecticidal activity against *N. lugens*. As to the activity against *S. litura*, it seemed that methyl group is favorable as R^3, and methylamino and *N*-formyl-*N*-methyl groups as R^1R^2N. Judging from the activities against these two insects, compound **17** is the most excellent among the compounds prepared. Acylated compounds frequently suffer deacylation in the metabolic pathways, but it is not clear if **17** is deformylated to **8**. This problem is now under investigation.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Atsuo Akayama for his assistance in the biological test, and helpful and stimulating discussions and suggestions.

REFERENCES

1) I. Minamida, K. Iwanaga, T. Tabuchi, H. Uneme, H. Dantsuji & T. Okauchi: *J. Pesticide Sci.* **18**, 31 (1993)
2) I. Minamida, K. Iwanaga, T. Tabuchi, I. Aoki, T. Fusaka, H. Ishizuka & T. Okauchi: *J. Pesticide Sci.* **18**, 41 (1993)
3) A. Binz & O. V. Schickh: *Berichte* **68B**, 315 (1935)
4) R. A. Crochet, Jr. & C. D. Blanton, Jr.: *Synthesis* **1974**, 55
5) H. E. Smith & V. Rajevsky: *J. Heterocycl. Chem.* **5**, 715 (1968)
6) H. E. Baumgarten, F. A. Bower, R. A. Setterquist & R. E. Allen: *J. Am. Chem. Soc.* **80**, 4588 (1958)
7) M. Tomizawa & I. Yamamoto: *J. Pesticide Sci.* **18**, 91 (1993)

要　　約

6-置換ピリジルアミノ基を有する非環状ニトロエテン化合物の合成と殺虫活性*

田渕学典，符阪隆文，岩永幸一
南田　勲，岡内哲夫

1-メチルアミノ-1-[*N*-メチル-*N*-(3-ピリジルメチル)]アミノ-2-ニトロエテン (**1**) の化学変換を行ないトビイロウンカに対する殺虫活性を調べた．最初に，化合物 **1** のメチレン部分を単結合，エチリデン，エチレンに変換し，単結合に変換した化合物 **3** が化合物 **1** 同様高い活性を示すことがわかった．次に，化合物 **3** のピリジン環の6位にメチル基，メトキシ基，塩素原子の導

入を行ない，クロロ体 (**8**) が最も良い結果を与えた．最後に，化合物 **8** の二つのメチル基の一方または両方の変換，および化合物 **8** のホルミル化を行ない，1-[*N*-(6–クロロ–3–ピリジル)–*N*–メチル] アミノ–1-(*N*–ホルミル–*N*–メチル) アミノ–2–ニトロエテン (**17**) がトビイロウンカのみならずハスモンヨトウに対しても優れた活性を示すことがわかった．

* 非環状ニトロエテン化合物の研究 (第 3 報)