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Original Article

Synthesis and Insecticidal Activity of *N*-(4-Aryloxybenzyl)-pyrazolecarboxamide Derivatives

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Thirty-eight derivatives of *N*-(4-aryloxybenzyl)pyrazolecarboxamide were synthesized and their insecticidal activity was examined. Among them *N*-[4-(4-trifluoromethylphenoxy)benzyl]-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide (**27**) was found to be potent insecticide against not only hemiptera insects but also lepidoptera insect. Insecticidal activity of its enantiomers is also discussed in this paper.

INTRODUCTION

In our previous paper, we have reported the structure-activity relationships of *N*-benzylpyrazole-5-carboxamide derivatives. Among them, *N*-(4-*tert*-butylbenzyl)-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide (tebufenpyrad, Pyranica®, MK-239) was the most effective acaricide.[1] The subsequent modification of tebufenpyrad has yielded *N*-(4-*tert*-butylbenzyl)-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide, whose activity was almost equal to that of tebufenpyrad.[2]

In the course of our study, in order to obtain potent insecticidal compounds, a series of *N*-(4-aryloxybenzyl)-pyrazolecarboxamide derivatives was synthesized and their insecticidal activity was examined.[3,4]

This paper describes the synthesis and the structure-activity relationships of insecticidal pyrazolecarboxamide derivatives.

MATERIALS AND METHODS

1. Synthesis of Compounds

The synthetic route of pyrazole derivatives is shown in Fig. 1.

Pyrazole-5-carboxylic acids (**Ia**),[5–8] 2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxylic acids (**Ib**) and 4, 5, 6, 7-tetrahydroindazole-3(2*H*)-carboxylic acids (**Ic**) were synthesized according to the literature.[9,10] Phenoxybenzylamines (**III**) were synthesized by reduction of the corresponding nitriles or oximes, or by hydrolysis of the corresponding phthalimides or isothiocyanates in the conventional way. For an example, the synthetic route of 4-(4-trifluoromethylphenoxy)benzylamine is shown in Fig. 2.

Reaction of pyrazolecarboxylic acids (**I**) with thionyl chloride gave acid chlorides (**II**). A number of new pyrazole derivatives (**IV**) were prepared by reacting the acid chlorides (**II**) with 4-phenoxybenzylamines (**III**) in the presence of triethylamine. Compounds **14** and **15** were prepared by oxidation of compound **11** with *m*-chloroperbenzoic acid in the known way.[11,12] The structures of compounds were confirmed by IR and ^{1}H NMR spectra. Melting points were measured with a Yanagimoto micromelting point apparatus and uncorrected. Refractive indexes were measured with an Atago Abbe-refractometer IT. Optical rotations were measured with a JASCO J-600 Spectropolarimeter. The followings are the typical synthetic procedures.

1.1 Preparation of 4-(4-trifluoromethylphenoxy)benzylamine

A mixture of sodium *p*-cresol (50.1 g, 0.39 mol), 4-chloro-α, α, α -trifluorotoluene (69.4 g, 0.39 mol), tris(3, 6-dioxaheptyl)amine (phase-transfer-catalyst; 13.9 g, 0.043 mol), copper(I) chloride (5.0 g, 0.05 mol) and anisole (250 ml) was heated under nitrogen atmosphere at 150°C for 6 hr. The reaction mixture was cooled, water (300 ml) was then added, and neutralized with hydrochloric acid. The organic layer was separated. After the solvent was removed under reduced pressure, the residue was purified by distillation (150°C/1 mmHg) to give 60.0 g (62%) of 4-methyl-4′-trifluoromethyldiphenyl ether as colorless crystals, mp 65–67°C. The diphenyl ether was prepared by the method of Soula.[13] Without adding the phase-transfer-catalyst, the yield of this compound was 6%.

A mixture of 4-methyl-4′-trifluoromethyldiphenyl ether (60.0 g, 0.24 mol), *N*-bromosuccinimide (42.4 g, 0.24 mol) and benzoylperoxide (1.94 g, 0.008 mol) in carbon

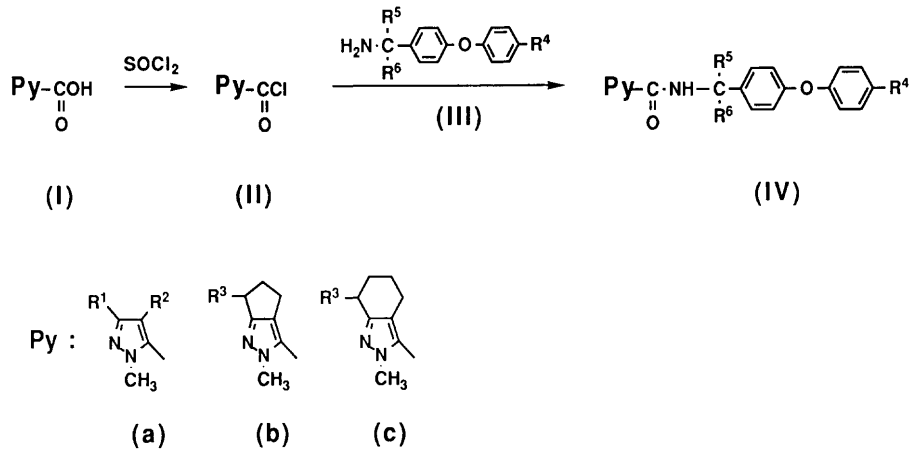


Fig. 1 Synthetic route of pyrazole derivatives (**IV**).

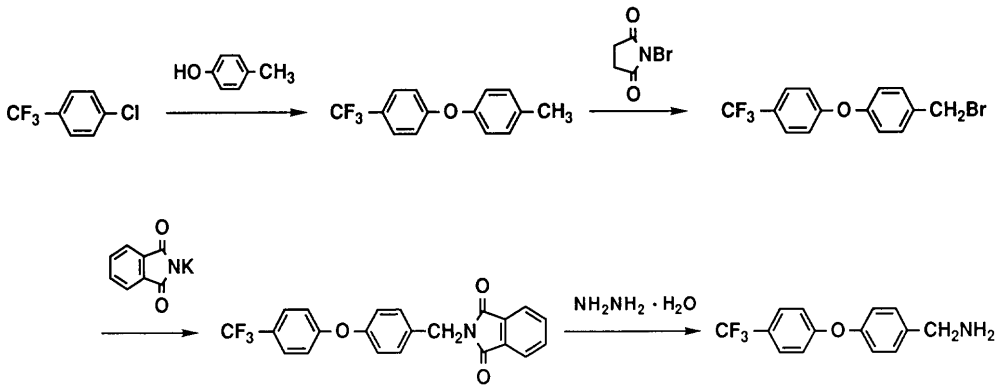


Fig. 2 Synthetic route of 4-(4-trifluoromethylphenoxy)benzylamine.

tetrachloride (230 ml) was heated under reflux for 1 hr. The reaction mixture was cooled, and succinimide formed during the reaction was removed by filtration. The filtrate was washed with a solution of sodium sulfite and then with a solution of sodium hydrogen carbonate. After the solvent was removed under reduced pressure, 81.2 g of light yellow oil, 4-(4-trifluoromethylphenoxy)-benzylbromide, was obtained.

A mixture of crude 4-(4-trifluoromethylphenoxy)benzylbromide (81.2 g) and potassium phthalimide (53.3 g, 0.29 mol) in 1-methyl-2-pyrrolidone (150 ml) was heated at 100°C for 3 hr. The reaction mixture was poured into a saturated solution of sodium chloride, and extracted with ethyl acetate (500 ml). After the organic layer was separated, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, eluted with hexane–chloroform (1 : 1) to give 60.0 g (64%) of *N*-[4-(4-trifluoromethylphenoxy)-benzyl]phthalimide as colorless crystals, mp 140–141°C.

A mixture of *N*-[4-(4-trifluoromethylphenoxy)benzyl]-phthalimide (57.8 g, 0.15 mol) and hydrazine monohydrate (15.0 g, 0.3 mol) in ethanol (500 ml) was heated under reflux for 1 hr. The reaction mixture was cooled, and phthalhydrazide formed was removed by filtration. The solvent was removed under reduced pressure to give 40.0 g of crude 4-(4-trifluoromethylphenoxy)benzylamine.

1.2 Preparation of pyrazolecarboxamides

1.2.1 Preparation of N-[4-(4-trifluoromethylphenoxy)-benzyl]-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide (27)

A mixture of 2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxylic acid (18.0 g, 0.1 mol) and thionyl chloride (17.8 g, 0.15 mol) was heated under reflux for 1 hr. The reaction mixture was then cooled, and after excess thionyl chloride was removed under reduced pressure, the residue was dissolved in toluene (200 ml). The obtained solution was added dropwise to a solution of 4-(4-trifluoromethylphenoxy)benzylamine (32.0 g, 0.12 mol) in toluene (100 ml) at 0–5°C in the presence of triethylamine (12.1 g, 0.12 mol). Then the mixture was stirred at room temperature for 2 hr, poured into ice water and extracted with toluene (100 ml). The organic layer was separated, washed twice with water (100 ml) and dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel, eluted with hexane–ethyl acetate (3 : 1), to give 38.6 g (90%) of **27** as colorless crystals, mp 74–75°C.

^{1}H NMR ($CDCl_3$) δ ppm : 1.30 (3H, d, J = 6 Hz), 2.0

(1H, m), 2.7 (3H, m), 3.1 (1H, m), 4.18 (3H, s), 4.60 (2H, d, J=6 Hz), 6.04 (1H, bs), 7.04 (4H, d, J=9 Hz), 7.35 (2H, d, J=7.5 Hz), 7.58 (2H, d, J=7.5 Hz). IR (KBr) cm^{-1}: 3310, 2970, 1640, 1505, 1320, 1245, 1065.

1.2.2 Preparation of N-[4-(4-methylthiophenoxy)benzyl]-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide (11)

A solution of 4-chloro-3-ethyl-1-methylpyrazole-5-carbonyl chloride (20.7 g, 0.1 mol) in toluene (150 ml) was added dropwise to a solution of 4-(4-methylthiophenoxy)benzylamine (24.5 g, 0.12 mol) in toluene (100 ml) at 0-5°C in the presence of triethylamine (12.1 g, 0.12 mol). Then the mixture was stirred at room temperature for 2 hr, poured into ice water and extracted with toluene (100 ml). The organic layer was separated, washed twice with water (100 ml) and dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel, eluted with hexane-ethyl acetate (3 : 1), to give 37 g (90%) of **11** as colorless crystals, mp 87-88°C.

^{1}H NMR ($CDCl_3$) δ ppm: 1.29 (3H, t, J=7.5 Hz), 2.49 (3H, s), 2.64 (2H, q, J=7.5 Hz), 4.16 (3H, s), 4.62 (2H, d, J=6 Hz), 6.86-7.12 (5H, m), 7.20-7.47 (4H, m).

1.2.3 Preparation of N-[4-(4-methylsulfinylphenoxy)benzyl]-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide (14)

A mixture of compound **11** (20.8 g, 0.05 mol) and *m*-chloroperbenzoic acid (8.6 g, 0.05 mol) in dichloromethane (200 ml) was stirred at room temperature for 5 hr. To the mixture was added 10% aqueous sodium sulfite solution (100 ml) and then stirred at room temperature for 1 hr. The organic layer was separated, washed twice with water (100 ml) and dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel, eluted with chloroform, to give 13.0 g (60%) of **14** as colorless crystals, mp 107-108°C.

^{1}H NMR ($CDCl_3$) δ ppm: 1.25 (3H, t, J=7.5 Hz), 2.64 (2H, q, J=7.5 Hz), 2.71 (3H, s), 4.15 (3H, s), 4.65 (2H, d, J=6 Hz), 6.98-7.27 (5H, m), 7.42 (2H, d, J=9 Hz), 7.66 (2H, d, J=9 Hz).

1.2.4 Preparation of N-[4-(4-methylsulfonylphenoxy)benzyl]-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide (15)

A mixture of **11** (20.8 g, 0.05 mol) and *m*-chloroperbenzoic acid (17.2 g, 0.1 mol) in dichloromethane (200 ml) was stirred at room temperature overnight. To the mixture was added 10% aqueous sodium sulfite solution (100 ml) and then stirred at room temperature for 1 hr. The organic layer was separated, washed twice with water (100 ml) and dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel, eluted with hexane-ethyl acetate (1 : 2), to give 20.2 g (90%) of **15** as colorless crystals, mp 78-79°C.

^{1}H NMR ($CDCl_3$) δ ppm: 1.24 (3H, t, J=7.5 Hz), 2.62 (2H, q, J=7.5 Hz), 3.03 (3H, s), 4.11 (3H, s), 4.66 (2H, d, J=6 Hz), 6.94-7.24 (5H, m), 7.42 (2H, d, J=9 Hz), 7.90 (2H, d, J=9 Hz).

1.2.5 Preparation of N-[4-(4-trifluoromethylphenoxy)-α-methylbenzyl]-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide (33 and 34)

A solution of 2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carbonyl chloride (19.9 g, 0.1 mol) in toluene (150 ml) was added dropwise to a solution of 4-(4-trifluoromethylphenoxy)-α-methylbenzylamine (33.7 g, 0.12 mol) in toluene (100 ml) at 0-5°C in the presence of triethylamine (12.1 g, 0.12 mol). Then the mixture was stirred at room temperature for 2 hr, poured into ice water and extracted with toluene (100 ml). The organic layer was separated, washed twice with water (100 ml) and dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel, eluted with hexane-ethyl acetate (2 : 1) to give 10.1 g (23%) of **34** as colorless crystals, mp 126-128°C and then 10.1 g (23%) of **33** as colorless crystals, mp 131-133°C. Compounds **33** and **34** are diastereomers.

^{1}H NMR ($CDCl_3$) δ ppm: Compound **33**: 1.28 (3H, d, J=6 Hz), 1.57 (3H, d, J=6 Hz), 2.0 (1H, m), 2.7 (3H, m), 3.1 (1H, m), 4.15 (3H, s), 5.25 (1H, m), 5.93 (1H, bs), 7.04 (4H, d, J=9 Hz), 7.38 (2H, d, J=9 Hz), 7.60 (2H, d, J=9 Hz); compound **34**: 1.28 (3H, d, J=6 Hz), 1.57 (3H, d, J= 6 Hz), 2.0 (1H, m), 2.7 (3H, m), 3.1 (1H, m), 4.14 (3H, s), 5.23 (1H, m), 5.93 (1H, bs), 7.04 (4H, d, J= 9 Hz), 7.38 (2H, d, J=9 Hz), 7.58 (2H, d, J=9 Hz).

1.2.6 Preparation of optically active compounds 31 and 32

Compound **27** (800 mg) was separated to enantiomers by HPLC [LC-908, Japan Analytical Industry Co.; column: Daicel CHIRALCELL OD, 20.0 mm i.d. ×500 mm; eluent: hexane-isopropyl alcohol (9 : 1)] to give 360 mg of **31** (50.5 min) as colorless crystals, mp 124-125°C, $[\alpha]_D^{20}$ +9.7° (c=1.0, $CDCl_3$) and then 340 mg of **32** (85.7 min) as colorless crystals, mp 124-125°C, $[\alpha]_D^{20}$ −9.9° (c=1.0, $CDCl_3$).

Optical purities of compounds **31** and **32** were measured by HPLC with Daicel CHIRALCELL OD (4.6 mm i.d. ×250 mm) and they were almost 100 and 99.3% ee, respectively.

2. Biological Tests

Tests described below were repeated twice for each concentration. The activity rating was expressed as indexes of 0 to 3, corresponding to 0-29, 30-79, 80-99 and 100% mortality respectively.

2.1 Hoppers

Five 3rd-instar larvae of either green rice leafhopper, *Nephotettix cincticeps*, or brown rice planthopper, *Nilaparavata lugens*, were released into each glass cylinder with 2 rice seedlings. Then the suspension prepared by diluting 20% wettable powder of a test compound with water to the predetermined concentrations was sprayed on both hoppers and plants. The treated hoppers were kept at 25°C during the test period. The mortality was observed 4 days after treatment for leafhoppers and 5 days after treatment for planthoppers (Tables 1–4).

2.2 Aphid

Two adults of green peach aphid, *Myzus persicae*, were released on a detached leaf of daikon. After 6 days, the leaf with adults and nymphs of aphid was dipped in the suspension mentioned above. The leaf was soaked in a bial filled with water to prevent from drying and kept at 25°C during the test period. The mortality was observed 4 days after treatment (Table 4).

2.3 Diamondback moth

A leaf disk of cabbage was dipped in the suspension mentioned above. Five 3rd-instar larvae of diamondback moth, *Plutella xylostella*, were maintained with the treated leaf disk in a plastic cap and kept at 25°C during the test period. The mortality was observed 4 days after treatment (Table 4).

2.4 Two spotted spider mite

Two spotted spider mite, *Tetranychus urticae*, and method used was the same as previously reported.[1)]

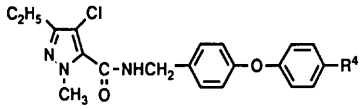
RESULT AND DISCUSSION

Table 1 shows some *N*-[4-(4-substituted phenoxy)benzyl]-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamides and their insecticidal activity against *Nephotettix cincticeps*. When R^4 was the alkyl group, compound having methyl group (**2**) showed 100% mortality against *Nephotettix cincticeps* at 12.5 ppm. However, substitution of the alkyl group longer than methyl group reduced the activity (**3**–**5**). *tert*-Butyl derivative (**5**) was inactive at 50 ppm. In addition, when R^4 was alkoxy or haloalkoxy group, the compounds having methoxy (**6**) or difluoromethoxy group (**8**) showed 100% mortality at 12.5 ppm. In the case of larger substituents (**7** and **9**), the activities decreased. Chloro derivative (**10**) was slightly more active than hydrogen derivative (**1**). Among alkylthio derivatives (**11**–**13**), methylthio derivative (**11**) was the most active. These findings indicate that small substituents such as methyl, methoxy, difluoromethoxy or methylthio group at the 4-position on the benzene ring increased the activity (**2**, **6**, **8** and **11**). And introduction of strong electron-withdrawing groups into the 4-position on the benzene ring resulted in high activity (**14**–**19**). Among them, difluoromethyl (**16**) and nitro derivatives (**19**) were the most active.

Table 2 shows the effect of substitution at the 3, 4-dipositions on the pyrazole ring (R^1, R^2). Some alkyl groups were introduced into the 3-position on the pyrazole ring (R^1). Among them, ethyl derivatives (**3** and **22**–**24**) were the most active. In the case of smaller (H, **20**; CH_3, **21**) or larger (i-C_3H_7, **25**) substituents, the activities decreased. When R^1 was ethyl group, compounds whose R^2 was hydrogen (**22**), fluoro (**23**), chloro (**3**) or bromine (**24**) atom showed almost the same rate of activities. Some bicyclic *N*-[4-(4-trifluoromethylphenoxy)benzyl]-2-methylpyrazole-3-carboxamides were also synthesized. Enlargement of five-membered ring to six-membered ring reduced the activity (**26**, **29** and **27**, **30**). This finding suggests that a ring of proper size is important for the insecticidal activity. Introduction of a methyl group into the 6-position of compound **26** resulted in the highest activity (**27**). Elongation of alkyl chain in compound **27**, on the other hand, reduced the activity (**28**).

Table 3 shows the insecticidal activity of the enantiomers and the effect of substitution at the benzyl

Table 1 *N*-[4-(4-Substituted phenoxy)benzyl]-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamides and their insecticidal activity against *Nephotettix cincticeps*.



No.	R^4	mp (°C)	Activity rating (ppm)		
			50	12.5	3.1
1	H	102–103	3	1	—[a)]
2	CH_3	87–89	3	3	1
3	C_2H_5	87–88	3	2	1
4	i-C_3H_7	86–88	2	1	—
5	t-C_4H_9	67–68	0	—	—
6	CH_3O	85–87	3	3	1
7	i-C_3H_7O	98–99	2	1	0
8	CHF_2O	69–70	3	3	2
9	CF_3CH_2O	81–82	3	1	—
10	Cl	110–112	3	2	2
11	CH_3S	87–88	3	3	2
12	C_2H_5S	Amorphous[b)]	3	2	1
13	i-C_3H_7S	Amorphous[c)]	3	1	1
14	CH_3SO	78–79	3	3	1
15	CH_3SO_2	107–108	3	3	1
16	CHF_2	129–130	3	3	3
17	CF_3	121–122	3	3	1
18	CN	105–107	3	3	0
19	NO_2	117–118	3	3	3

a) Not tested.

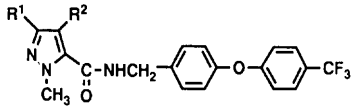
b) ^{1}H NMR ($CDCl_3$) δ ppm: 1.24 (3H, t, J=7.5 Hz), 1.29 (3H, t, J=7.5 Hz), 2.64 (4H, m), 4.15 (3H, s), 4.61 (2H, d, J=6 Hz), 6.98 (4H, m), 7.05 (1H, bs), 7.34 (4H, m).

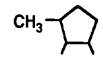
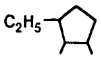
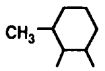
c) ^{1}H NMR ($CDCl_3$) δ ppm: 1.24 (3H, t, J=7.5 Hz), 1.27 (6H, d, J=6 Hz), 2.63 (2H, q, J=7.5 Hz), 3.28 (1H, m, J=6 Hz), 4.15 (3H, s), 4.62 (2H, d, J=6 Hz), 6.94 (2H, d, J=7.5 Hz), 7.00 (2H, d, J=9 Hz), 7.05 (1H, bs), 7.33 (2H, d, J=9 Hz), 7.40 (2H, d, J=7.5 Hz).

position of compound **27**. (+)-Enantiomer **31** was a quarter as active as (−)-enantiomer **32**, which was slightly more active than the racemic compound **27**. The crystal structures of enantiomers (**31** and **32**) determined by X-ray crystallographic analysis will be reported in the future. In replacement of the methylene group, an ethylidene (**33** and **34**) or an isopropylidene group (**35**) was introduced to compound **27**. Introduction of one or two methyl group into the methylene group of compound **27** reduced the activity. Compounds **33** and **34** are diastereomers and they showed no difference in the activity. But no activity was observed concerning compound **35**.

Table 4 shows the biological activity of representative compounds of this study, tebufenpyrad (*N*-(4-*tert*-butylbenzyl)-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide) (**39**) and *N*-(4-*tert*-butylbenzyl)-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide (**40**). Compounds **39** and **40** were potent acaricides, but they were little active against insects. On the other hand, compounds **27** and **36**–**38** showed high activity against not only insects but also spider mite. Among

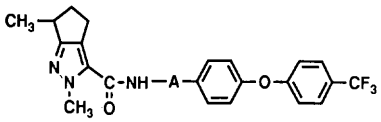
Table 2 *N*-[4-(4-Trifluoromethylphenoxy)benzyl]-3, 4-disubstituted-1-methylpyrazole-5-carboxamides and their insecticidal activity against *Nephotettix cincticeps*.



No.	R^1	R^2	mp (°C)	Activity rating (ppm)			
				50	12.5	3.1	0.8
20	H	Cl	95–96	3	2	1	—[a]
21	CH_3	Cl	132–133	3	2	2	1
22	C_2H_5	H	78–80	3	3	1	—
23	C_2H_5	F	64–65	3	3	1	0
3	C_2H_5	Cl	121–122	3	3	1	1
24	C_2H_5	Br	133–134	3	3	1	1
25	*i*-C_3H_7	Cl	117–119	2	2	1	—
26			131–133	3	3	3	0
27			74–75	3	3	3	1
28			95–96	3	3	1	0
29			137–138	3	2	2	0
30			141–143	3	3	0	0

a) Not tested.

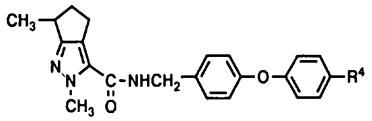
Table 3 *N*-[4-(4-Trifluoromethylphenoxy)benzyl]-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamides and their insecticidal activity against *Nephotettix cincticeps*.



No.	A	mp (°C) or n_D (°C)	Activity rating (ppm)			
			50	12.5	3.1	0.8
27	CH_2	74–75	3	3	3	1
31[a]	CH_2	124–125	3	3	1	—[e]
32[b]	CH_2	124–125	3	3	3	2
33[c]	$CH(CH_3)$	131–133	3	3	2	0
34[d]	$CH(CH_3)$	126–128	3	3	2	0
35	$C(CH_3)_2$	1.5427(25)	0	—	—	—

[a] $[\alpha]_D^{20}+9.7°$. [b] $[\alpha]_D^{20}-9.9°$. [c] Compounds **33** and **34** are diastereomers. Low *Rf* value in TLC. [d] High *Rf* value in TLC. [e] Not tested.

Table 4 Biological activity of *N*-[4-(4-substituted phenoxy)benzyl]-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamides and their related compounds.



No.	R^4	mp (°C) or n_D(°C)	Activity rating (ppm)												
			N. c.[a]			*N. l.*[b]			*M. p.*[c]			*P. x.*[d]			*T. u.*[e]	
			12.5	3.1	0.8	12.5	3.1	0.8	12.5	3.1	0.8	12.5	3.1	0.8	12.5	3.1
27	CF_3	74–75	3	3	1	3	3	3	3	3	3	3	2	0	3	3
36	SCH_3	117–118	3	2	1	2	1	1	3	3	0	3	2	0	3	2
37	CN	128–129	1	0	—[f]	3	2	2	3	2	0	3	3	1	3	3
38	NO_2	1.5850(24)	3	3	1	2	2	0	3	3	1	3	3	0	2	1
39	Tebufenpyrad[g]	61–62	0	—	—	0	—	—	1	—	—	0	—	—	3[i]	3[i]
40	—[h]	1.5465(24.5)	1	—	—	0	—	—	0	—	—	0	—	—	3[j]	3[j]

[a] *Nephotettix cincticeps*. [b] *Nilaparavata lugens*. [c] *Myzus persicae*. [d] *Plutella xylostella*. [e] *Tetranychus urticae*. [f] Not tested. [g] *N*-(4-*tert*-Butylbenzyl)-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide (tebufenpyrad). [h] *N*-(4-*tert*-Butylbenzyl)-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide. [i] Data were taken from Table 5 in our previous paper.[1] [j] Data were taken from Table 4 in our previous paper.[2]

them, trifluoromethyl (**27**) and nitro (**38**) derivatives were highly active at 3.1 ppm against *Nephotettix cincticeps*. Especially, compound **27** showed 100% mortality at 0.8 ppm against both *Nilaparavata lugens* and *Myzus persicae*. And compounds **27** and **36**–**38** showed potent activity against not only hemiptera insects but also lepidoptera insect such as *Plutella xylostella*. Among them, cyano (**37**) and nitro (**38**) derivatives were more active than trifluoromethyl (**27**) and methylthio (**36**) derivatives against *Plutella xylostella*.

As mentioned above, to obtain new insecticidal compounds, thirty-eight derivatives of *N*-(4-aryloxybenzyl)-pyrazolecarboxamide were synthesized. Among them, *N*-[4-(4-trifluoromethylphenoxy)benzyl]-2, 6-dimethyl-2, 4, 5, 6-tetrahydrocyclopentapyrazole-3-carboxamide (**27**) was found to be potent insecticide against not only hemiptera insects but also lepidoptera insect.

The compound **27** showed rapid activity and its speed of action was about equal to that of the organophosphate insecticide.

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要　　約

N-(4-アリールオキシベンジル)ピラゾールカルボキサミド誘導体の合成と殺虫活性

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われわれはさきに *N*-(4-*tert*-ブチルベンジル)-4-クロロ-3-エチル-1-メチルピラゾール-5-カルボキサミド (tebufenpyrad) および *N*-(4-*tert*-ブチルベンジル)-2, 6-ジメチル-2, 4, 5, 6-テトラヒドロシクロペンタピラゾール-3-カルボキサミドが高い殺ダニ活性を有することを報告した．本研究では，新しい殺虫活性化合物を得ることを目標に38種の *N*-(4-アリールオキシベンジル)ピラゾール誘導体(**IV**)を合成し，殺虫活性を試験した．なかでも *N*-[4-(4-トリフルオロメチルフェノキシ)ベンジル]-2, 6-ジメチル-2, 4, 5, 6-テトラヒドロシクロペンタピラゾール-3-カルボキサミド (**27**) が，ツマグロヨコバイのみならずトビイロウンカやモモアカアブラムシに対してももっとも高い活性を示した．また，本化合物は鱗翅目害虫であるコナガに対しても高活性を示した．