J. Pesticide Sci. **15**, 531–538 (1990)

Original Article

Selective Herbicidal Activities of Ethyl 5-(4,6-Dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate and Its Related Compounds

Susumu YAMAMOTO, Toshiaki SATO, Yoshihiro IWASAWA,
Fumio SUZUKI, Takashi IKAI,* Koichi SUZUKI*
and Tsutomu NAWAMAKI*

Central Research Institute, Nissan Chemical Ind., Ltd., Tsuboi-cho, Funabashi 274, Japan
**Shiraoka Research Station of Biological Science, Nissan Chemical Ind., Ltd.,*
Shiraoka-cho, Minamisaitama-gun, Saitama 349–02, Japan

(Received February 1, 1990)

Twenty-six derivatives of pyrazole-5-sulfonylureas were synthesized and investigated for their herbicidal activities. The title compound, pyrazosulfuron-ethyl (**5**, code No. NC-311), was found the best compound that was highly effective in controlling paddy weeds, especially annual and perennial broad-leaf weeds and sedges. In the paddy-field trial, **5** effectively controlled weeds at the rate of 20–30 g a.i./ha without phytotoxicity to transplanted rice. This herbicide is proposed as a potent novel herbicide to protect paddy rice.

INTRODUCTION

Sulfonylurea herbicides such as chlorsulfuron and sulfometuron-methyl are a new class of compounds that have both pre- and post-emergence herbicidal activities at extremely low application rates (Fig. 1).[1-3] We are interested in their structures and herbicidal activities and attempted to develop new compounds with high activity as well as excellent crop safety.

Sulfonylurea compounds have three moieties, an aryl group, a sulfonylurea bridge and a heterocyclic moiety (Fig. 1).[2] The aryl group is known to retain the herbicidal activity even when heterocycles such as thiophene and pyridine are introduced replacing the aryl group,[4,5] but structural modification of the other moieties generally reduces the activity.

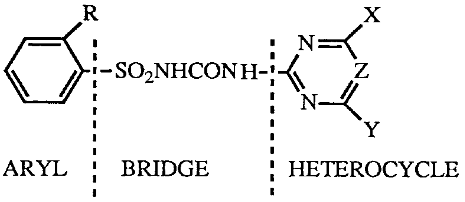
Hence, we first replaced the aryl group with several kinds of azoles, such as imidazole, oxazole, thiazole, pyrazole, isoxazole and isothiazole, which were chosen because those moieties are often used in pharmaceuticals,[6] agricultural chemicals[7] and biologically active natural products such as histamine and vitamin B_1. We examined their herbicidal activities and found sulfonylurea compounds having pyrazole moieties (pyrazolesulfonylureas) were most potent. Then, we extensively investigated a series of pyrazolesulfonylureas and found that several compounds, in which the sulfonylurea bridge was binded to the 5-position of the pyrazole ring (pyrazole-5-sulfonylureas (**I**)), had selectivity of rice plants from paddy weeds (Fig. 2).[8-10] Among them, ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate, pyrazosulfuron-ethyl (NC-311) (**5**), was the most effective rice herbicide.[11-13]

This paper describes the synthesis and herbicidal activity of **I**. The herbicidal properties and the field-test result of compound **5** are also described.

MATERIALS AND METHODS

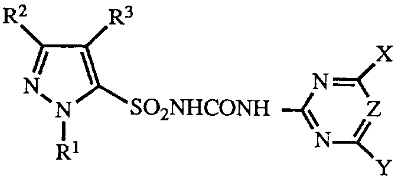
1. Apparatus

^1H and ^{13}C NMR spectra were recorded on a



Chlorsulfuron: R=Cl, X=Me, Y=OMe, Z=N
Sulfometuron-methyl: R=CO_2Me, X,Y=Me, Z=CH

Fig. 1 The structure of sulfonylurea herbicides.



(I)

R^1: H, Alkyl, Phenyl R^2, R^3: various substituents
X,Y: Me, OMe Z: CH, N
Pyrazosulfuron-ethyl (**5**): R^1=Me, R^2=H, R^3=CO_2Et
X,Y=OMe, Z=CH

Fig. 2 The structure of pyrazole-5-sulfonylureas.

JEOL FX-90Q spectrometer with tetramethylsilane as an internal reference. IR spectra were measured on a DIGILAB FTS-40 Infrared Spectrometer. Mass spectra were measured on a DX-300, JMA-3100. All melting points are uncorrected.

2. *Syntheses of Compounds*

2.1 *Preparation of pyrazole-5-sulfonamides (**IV**)* (General procedure)[8,9,14]

Method A: 5-Aminopyrazoles (**II**) in hydrochloric acid were diazotized with sodium nitrite and the resulting diazonium salts were poured into a mixture of sulfur dioxide and a catalytic amount of cupric chloride or cupric sulfate in acetic acid at 0–20°C, affording pyrazole-5-sulfonyl chlorides (**III**). Compounds **III** were reacted with aqueous ammonia to obtain **IV**.

Method B: Lithium pyrazole-5-sulfinates (**VI**) were prepared from 5-unsubstituted pyrazoles (**V**) *via* lithiation with butyllithium or lithium diisopropylamide at −60°C, followed by the reaction with sulfur dioxide. Compounds **VI** were chlorinated with *N*-chlorosuccinimide to yield **III**. Compounds **III** were converted to **IV** with aqueous ammonia.

Method C: Pyrazole-5-thiols (**VIII**) were prepared from 5-chloropyrazoles (**VII**) with sodium hydrosulfide in dimethylformamide at 60–80°C. Compounds **VIII** were converted to **III** *via* oxidative chlorination with chlorine in aqueous acetic acid at 10–25°C. Compounds **III** were reacted with aqueous ammonia to obtain **IV**.

Compounds **IV** for the syntheses of compounds **1**–**7**, **13**, **14**, **20**–**26**, compounds **8**–**11** and compounds **12**, **15**–**19** were prepared by methods A, B and C respectively. These reactions are shown in Fig. 3.

2.2 *Preparation of pyrazole-5-sulfonylureas (**I**)*[8,9]

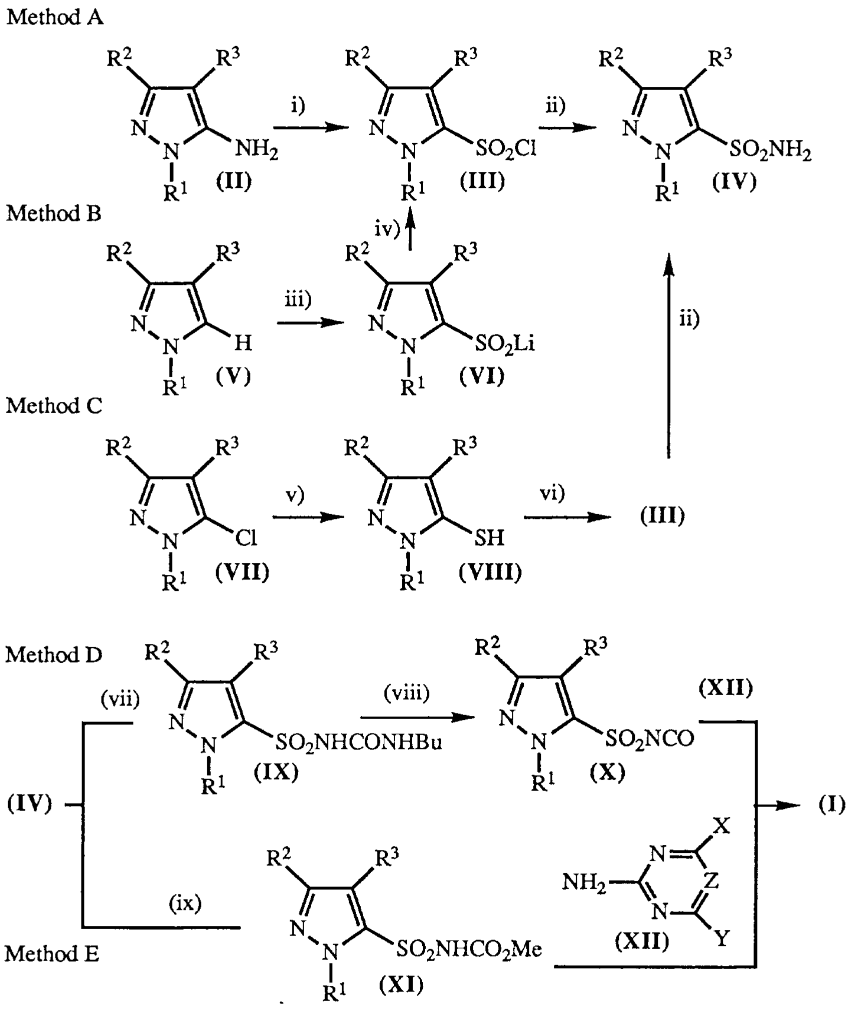
Method D: Pyrazole-5-sulfonylisocyanates (**X**) were prepared from pyrazole-5-sulfonamides (**IV**) *via* *N*-(butylcarbamoyl)pyrazole-5-sulfonamides (**IX**) according to the literature.[5] Pyrazole-5-sulfonylureas (**I**) were synthesized by adding compounds **X** to a suspension of aminopyrimidine or aminotriazine derivatives (**XII**) in an inert solvent such as acetonitrile, ether or benzene. After stirring for few hours at room temperature, the resulting solid was collected and washed with acetonitrile or benzene to obtain **I**.

Method E: Pyrazole-5-sulfonylcarbamates (**XI**) were prepared from compounds **IV** by the reaction with methyl chloroformate in the presence of potassium carbonate. Compounds **XI** were condensed with **XII** in an inert solvent such as toluene or xylene at 80–90°C while generated methanol was removed under reduced pressure to afford **I**. A typical example for the preparation of compounds **I** from compounds **II** is given below.

2.3 *Preparation of ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (**5**) (pyrazosulfuron-ethyl)*

2.3.1 *Ethyl 1-methyl-5-sulfamoylpyrazole-4-carboxylate **IV** (R^1=Me, R^2=H, R^3=CO_2Et)*

Ethyl 5-amino-1-methylpyrazole-4-carboxylate **II** (R^1=Me, R^2=H, R^3=CO_2Et; 16.9 g, 0.1 mol) was diazotized in a mixture of 63% sulfuric acid (46.7 g, 0.3 mol), 35% hydrochloric acid (11.0 g, 0.105 mol) and acetic acid (26 ml) by adding dropwise a solution of



i) 1. $NaNO_2$, HCl 2. SO_2, $CuCl_2$ ii) NH_4OH iii) 1. BuLi or i-Pr_2NLi 2. SO_2
iv) N-Chlorosuccinimide v) NaSH vi) Cl_2, H_2O vii) 1. BuNCO, K_2CO_3 2, HCl
viii) $COCl_2$ ix) 1. $ClCO_2Me$, K_2CO_3 2. HCl

Fig. 3 Synthetic routes of pyrazole-5-sulfonylureas.

sodium nitrite (8.3 g, 0.12 mol) in water (15 ml) at below 10°C. The diazo solution was stirred for 30 min and urea (1.2 g, 0.02 mol) was added to the solution to remove excess nitrous acid. After stirring for 30 min, the diazo solution was poured portionwise at 0–5°C into a mixture of sulfur dioxide (38.4 g, 0.6 mol), cupric chloride (0.2 g) and acetic acid (52 ml), and stirring was continued for 1 hr at 10°C. Then, water (70 ml) and 1,2-dichloroethane (56 ml) were added to the mixture, and the organic layer was separated and washed with water (50 ml) to obtain a solution that contained crude oil of **III** (R^1=Me, R^2=H, R^3=CO_2Et). After removal of remaining sulfur dioxide under reduced pressure, 28% aqueous ammonia (15.2 g, 0.25 mol) was added dropwise to the solution at 10°C and the mixture was stirred for 5 hr at room temperature. The organic layer was separated, washed with water (10 ml) and dried *in vacuo* to obtain 21.0 g crude solid of **IV** (R^1=Me, R^2=H, R^3=CO_2Et). Recrystallization of the solid from toluene gave 18.2 g (78% from **II**) of **IV** (R^1=Me, R^2=H, R^3=CO_2Et) as white crystalline solid, mp 113–114°C. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 1.38 (3H, t, J=7.0 Hz, $O\text{-}CH_2\text{-}C\underline{H}_3$), 4.17 (3H, s, $N\text{-}CH_3$), 4.35 (2H, q, J=7.0 Hz, $O\text{-}C\underline{H}_2\text{-}CH_3$), 6.40 (2H, bs, NH_2), 7.88 (1H, s, pyraz-H). ^{13}C NMR $\delta_{TMS}^{CDCl_3}$ ppm: 14.2 (q), 40.7 (q), 61.7 (t), 113.5 (s), 140.7 (d), 143.2 (s), 163.0 (s). IR ν_{max}^{KBr} cm^{-1}: 3320 (NH), 1700 (C=O), 1355 (SO_2), 1165 (SO_2). MS m/z: 233 (M^+), 205, 188. Found: C, 36.02; H, 4.71; N, 18.12, Calcd. for $C_7H_{11}N_3O_4S$: C, 36.05; H, 4.75; N, 18.01%.

*2.3.2 Ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (**5**)*

To a suspension of ethyl 1-methyl-5-sulfamoylpyrazole-4-carboxylate **IV** (R^1=Me, R^2=H, R^3=CO_2Et; 10.0 g, 42.9 mmol) and anhydrous potassium carbonate (8.9 g, 64.5 mmol) in acetonitrile (80 ml) was added *n*-butylisocyanate (4.9 g, 49.5 mmol) at room temperature. After stirring for 1 hr at room temperature, the reaction mixture was refluxed for 2 hr. After removal of the solvent, the residue was dissolved in cold water and a small amount of insoluble solid was filtered off. The filtrate was acidified with 35% hydrochloric acid, and the resulting solid was collected, washed with water and dried *in vacuo* to obtain 12.8 g (90%) of **IX** (R^1=Me, R^2=H, R^3=CO_2Et). Next, phosgene (5.2 g, 52.5 mmol) was introduced to a solution of **IX** in toluene (50 ml) at 100–110°C for 2 hr and the mixture was gently refluxed for 1 hr. After removal of excess phosgene and the solvent under reduced pressure, crude oil of **X** (R^1=Me, R^2=H, R^2=CO_2Et) was obtained. Compound **X** (R^1=Me, R^2=H, R^3=CO_2Et) was added dropwise to a solution of **XII** (X, Y=OMe, Z=CH) (5.1 g, 32.9 mmol) in benzene (30 ml) at room temperature. After stirring for 3 hr, the resulting solid was collected and recrystallized from benzene to obtain 11.2 g (70% from **IX**) white crystalline solid of **5**, mp 181–182°C. ^1H NMR $\delta_{TMS}^{CDCl_3}$ ppm: 1.30 (3H, t, J=7.1 Hz, O–CH_2–$\underline{CH_3}$), 4.03 (6H, s, O–CH_3), 4.24 (2H, q, J=7.1 Hz, O–$\underline{CH_2}$–CH_3), 4.34 (3H, s, N–CH_3), 5.80 (1H, s, pyrim-H), 7.31 (1H, bs, NH), 7.87 (1H, s, pyraz-H), 12.95 (1H, bs, NH). ^{13}C NMR $\delta_{TMS}^{CDCl_3}$ ppm: 14.1 (q), 41.4 (q), 54.9 (q), 60.9 (t), 85.4 (d), 116.1 (s), 138.6 (s), 140.2 (d), 149.6 (s), 155.2 (s), 160.6 (s), 171.6 (s). IR ν_{max}^{KBr} cm^{-1}: 3300 (NH), 1720 (C=O), 1608 (C=C, C=N), 1354 (SO_2), 1212 (C–O–C), 1155 (SO_2). MS m/z: 415 (MH^+), 214, 182, 156. Found: C, 40.57; H, 4.35; N, 20.20, Calcd. for $C_{14}H_{18}N_6O_7S$: C, 40.58; H, 4.38; N, 20.28%.

3. Biological Tests

3.1 Greenhouse test

A greenhouse test was conducted to examine preemergence activities of 26 compounds under a paddy condition to four weed species and transplanted rice, *Echinochloa crus-galli*, *Scirpus juncoides*, *Monochoria vaginalis*, *Rotala indica* and *Oryza sativa*

Plastic beakers (200 ml) 40 cm^2 in size were filled with clay loam soil (clay 18.0%, total carbon 0.51%, pH 6.18) and water was added up to 3 cm in depth. Weed seeds were sown on the soil surface and rice seedlings at the 2.5-leaf stage were transplanted. The next day a diluted suspension of wettable powder of each compound was applied to the flood water. After 18 days the herbicidal activity was assessed by the following ratings, 5: growth inhibition of more than 90% (substantial suppression), 4: growth inhibition of 70 to 90%, 3: growth inhibition of 40 to 70%, 2: growth inhibition of 20 to 40%, 1: growth inhibition of 5 to 20%, zero: growth inhibition of less than 5% (nonherbicidal effect).

*3.2 Herbicidal spectrum of compound **5***

The herbicidal activity of **5** was examined in a greenhouse on seven paddy weed species, *Echinochloa crus-galli*, *Scirpus juncoides*, *Monochoria vaginalis*, *Alisma canaliculatum*, *Sagittaria pygmaea*, *Cyperus scrotinus* and *Eleocharis kuroguwai*.

Plastic pots (1.3 *l*) 11.3 cm in diameter were filled with clay loam soil and water was added up to 4 cm in depth. In preemergence application, one or two days after planting weed seeds or tubers, **5** in a diluted suspension of wettable powder was applied to the flood water. Postemergence application was done 7–15 days after planting in the same way. Between 25 to 35 days after treatment, the fresh weight was measured and the dose for 75% control of each weed species (I_{75}) was calculated.

3.3 Field trial for transplanted rice

A field trial was aimed to examine the efficacy of **5** against paddy weeds and to confirm the safety for transplanted rice. The test was done in a heavy-clay field in Shiraoka, Saitama prefecture (clay 46.6%, silt 34.6%, sand 18.8%, total carbon 3.9%, pH 5.4). The field was puddled and leveled on June 3, 1983, and rice seedlings (cv. Musashi-Kogane) at the three-leaf stage were transplanted on June 7. The plot was 1 m^2 and the treatment was replicated three times. Granular **5** (**5** 0.1%, polyvinyl alcohol 1.5%, bentonite 20.0%, talc 78.4%) was applied 3 and 7 days after transplanting at a rate of 20 g a.i./ha, and after 3, 7, 10 and 15 days at 30 g a.i./ha. Butachlor, reference herbicide, was also applied in a granular formulation at 1500 g a.i./ha. One month after each application, the efficacy was evaluated by visual rating (0–100). The height and the number of tillers of rice were measured 32 days after transplanting.

RESULTS AND DISCUSSION

1. *Syntheses*

Only one report was available on the synthesis of **III** (R^1=Ph, R^2=Me, R^3=Cl) from **VIII** *via* pyrazole-5-sulfonic acid derivative,[15] and our work started to find facile and efficient methods for the syntheses of novel pyrazole-5-sulfonyl chlorides (**III**). We developed three methods, A, B and C, as described in Fig. 3. By method A, the procedure for the syntheses of phenylsulfonyl chlorides from corresponding anilines *via* diazonium salts[16] could be applied to the syntheses of **III** from 5-aminopyrazoles (**II**). By method B, 5-lithiated pyrazoles,[17] prepared from 5-unsubstituted derivatives **V**, were reacted with sulfur dioxide to give lithium sulfinates **VI**, which were chlorinated with *N*-chlorosuccinimide to afford **III**. By method C, oxidative chlorination of pyrazole-5-thiols (**VIII**) readily proceeded to give **III** with above 80% yields. This reaction had advantages of high yields and fewer reaction steps compared with the known method.[15] Thus, 22 derivatives of compounds **III** were prepared by the most suitable method of the three and reacted with aqueous ammonia to obtain **IV** with quantitative yields.

To synthesize pyrazole-5-sulfonylureas (**I**) except **3**, methods D and E were investigated as mentioned in *2.2*. Compound **3** was prepared by the hydrolysis of **5** in an aqueous basic condition.

2. *Biological Activity*

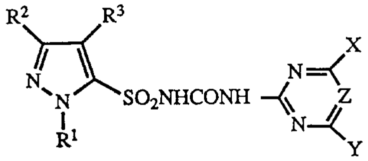
The herbicidal activity of **I** differed delicately according to the kind, number and position of substituent groups on the pyrazole ring (Table 1). In substituents R^1 at the 1-position of the pyrazole ring, methyl derivatives such as **4**, **5** and **6** showed the highest activity as well as good selectivity. Elongation of alkyl chain in **21** and **22** reduced the activity. Hydrogen and phenyl derivatives (**20** and **23**) showed lower activity. In substituents R^2 at the 3-position of the pyrazole ring, hydrogen, methyl, chlorine and methoxy derivatives such as **5**, **6**, **8** and **11** showed excellent activity and selectivity, whereas ethyl, trifluoromethyl, nitro and ester derivatives such as **7**, **9**, **10** and **12** insufficient activity. In substituents R^3 at the 4-position of the pyrazole ring, lower alkyl ester and dimethylsulfamoyl derivatives had the highest activity, whereas the carboxylic acid, carbamoyl, cyano and nitro derivatives gave no activity. A dimethylsulfamoyl derivative (**16**) was extremely phytotoxic to rice plants in sharp contrast to ester derivatives such as **4**, **5** and **6** that had excellent selectivity. Methyl, bromine and propanoyl derivatives such as **1**, **2** and **19** also showed selectivity and moderate activity.

As for another heterocyclic portion of molecular structure of **I**, replacement of the pyrimidine ring of **5** by the corresponding triazine ring as in **26** resulted in a complete loss of the herbicidal activity. Conversion of one or both of the methoxy groups on the pyrimidine ring to methyl as in **24** and **25** reduced the activity.

On the basis of the above result, **5** and **6** were selected as highly effective compounds, and after subsequent tests at high application rates to examine their phytotoxicity to rice plants, compound **5** (pyrazosulfuron-ethyl) was selected for further trials.

Table 2 shows the herbicidal activity of **5** against seven species of noxious paddy weeds in Japan. Doses for 75% weed control in preemergence application were less than 10 g a.i./ha for all weeds except *E. crus-galli*. The I_{75} value was less than 1 g a.i./ha against *C. serotinus*. In postemergence application, the I_{75} was less than 13 g a.i./ha against all weeds except *E. crus-galli*. Thus, **5** was found to be highly effective against major paddy weeds including perennials in both pre- and post-

Table 1 Pyrazole-5-sulfonylureas and their preemergence herbicidal activities under a paddy condition.



Compound								Activity[a]				
No.	R^1	R^2	R^3	X	Y	Z	mp (°C)	a	b	c	d	e[b]
1	Me	H	Me	OMe	OMe	CH	199–201	2	2	3	4	0
2	Me	H	Br	OMe	OMe	CH	198–200	0	3	4	3	0
3	Me	H	CO$_2$H	OMe	OMe	CH	202–204	0	0	0	0	0
4	Me	H	CO$_2$Me	OMe	OMe	CH	141–143	3	4	5	5	0
5	Me	H	CO$_2$Et	OMe	OMe	CH	181–182	3	5	5	5	0
6	Me	Me	CO$_2$Et	OMe	OMe	CH	144–146	4	5	5	5	0
7	Me	Et	CO$_2$Et	OMe	OMe	CH	148–150	2	3	4	5	0
8	Me	Cl	CO$_2$Et	OMe	OMe	CH	169–170	2	4	5	5	0
9	Me	CF$_3$	CO$_2$Et	OMe	OMe	CH	145–147	0	0	0	2	0
10	Me	NO$_2$	CO$_2$Et	OMe	OMe	CH	148–150	0	1	2	4	1
11	Me	OMe	CO$_2$Et	OMe	OMe	CH	142–143	3	4	5	5	0
12	Me	CO$_2$Et	CO$_2$Et	OMe	OMe	CH	150–152	0	0	0	0	0
13	Me	H	CO$_2$Pr	OMe	OMe	CH	167–168	0	4	5	5	0
14	Me	H	CO$_2$Bu	OMe	OMe	CH	125–128	0	0	0	0	0
15	Me	H	CONMe$_2$	OMe	OMe	CH	200–202	0	0	0	0	0
16	Me	H	SO$_2$NMe$_2$	OMe	OMe	CH	183–185	3	5	4	5	5
17	Me	H	CN	OMe	OMe	CH	177–178	0	0	0	0	0
18	Me	H	NO$_2$	OMe	OMe	CH	194–196	0	0	0	0	0
19	Me	H	COEt	OMe	OMe	CH	178–180	1	2	3	3	0
20	H	H	CO$_2$Et	OMe	OMe	CH	189–191	1	4	4	4	1
21	Et	H	CO$_2$Et	OMe	OMe	CH	157–159	1	4	5	5	1
22	Bu	H	CO$_2$Et	OMe	OMe	CH	173–175	0	0	0	0	0
23	Ph	H	CO$_2$Et	OMe	OMe	CH	183–185	0	2	3	4	0
24	Me	H	CO$_2$Et	Me	Me	CH	163–165	0	0	0	3	1
25	Me	H	CO$_2$Et	Me	OMe	CH	152–154	1	4	4	5	0
26	Me	H	CO$_2$Et	OMe	OMe	N	142–144	0	0	0	0	1

[a] The dose of each compound is 5 g a.i./ha.

[b] a, *Echinochloa crus-galli*; b, *Scirpus juncoides*; c, *Monochoria vaginalis*; d, *Rotala indica*; e, *Oryza sativa* (rice).

Table 2 Herbicidal activity of pyrazosulfuron-ethyl (**5**) against paddy weeds in a greenhouse test.

Weed species	I$_{75}$ value[a] (g a.i./ha)	
	Pre	Post
Echinochloa crus-galli	13	18 (1.5 *l*)[b]
Scirpus juncoides	8.3	13 (2 *l*)
Monochoria vaginalis	2.7	2.7 (3–5 *l*)
Alisma canaliculatum	2.1	1.4 (3–4 *l*)
Sagittaria pygmaea	1.9	2.7 (2 *l*)
Cyperus serotinus	0.9	1.9 (3–4 *l*)
Eleocharis kuroguwai	1.9	7.4 (10–20 cm)[c]

[a] Dose of 75% control. [b] Leaf stage of each weed. [c] Plant height.

emergence applications.

As the last step a field trial was conducted to evaluate whether **5** was an effective herbicide on transplanted rice in paddy. The result is summarized in Table 3. The compound showed excellent herbicidal activity against paddy weeds except *E. crus-galli* at 20–30 g a.i./ha at every application without causing any phytotoxicity to rice plants. It was also highly effective against *E. crus-galli* when applied early. The reference herbicide (butachlor) showed high activity against *E. crus-galli*, *S. juncoides* and broad-leaf weeds, but the activity was insufficient against *M.*

Table 3 The field trial of pyrazosulfuron-ethyl for transplanted rice in 1983.

	Application timing[a]	Weed control (%)[b]						Rice growth (%)[d]	
		a	b	c	d	e	f[c]	Plant height	No. of tillers
Pyrazosulfuron-ethyl	+3	98	97	100	100	95	98	104	100
20 g a.i./ha	+7	98	100	100	100	98	100	107	96
30 g a.i./ha	+3	97	100	100	100	97	100	104	99
	+7	98	100	100	100	98	100	104	100
	+10	90	93	93	100	95	97	102	101
	+15	85	97	97	100	95	97	101	105
Butachlor	+3	98	100	90	100	27	63	106	99
1500 g a.i./ha	+7	100	88	43	83	20	70	103	93
Hand weeding	—	—	—	—	—	—	—	100 35.7 cm	100 15.6/hill

[a] Days after transplanting.

[b] Growth inhibition: 100, 100% kill; zero, no effect.

[c] a, *Echinochloa crus-galli*; b, *Scirpus juncoides*; c, *Monochoria vaginalis*; d, Broad-leaf weeds; e, *Sagittaria pygmaea*; f, *Cyperus serotinus*.

[d] No significant differences were found among treated plots of pyrazosulfuron-ethyl and hand-weeding plots at a 5% level of *t*-test.

vaginalis and *S. pygmaea* at 1500 g a.i./ha. The result of the field trial supports that pyrazosulfuron-ethyl (**5**) has high activity and good selectivity in practical use.

ACKNOWLEDGMENTS

We wish to express our thanks to Dr. Yasukazu Ura, Managing Director of Nissan Chemical Ind., Ltd., Mr. Kunihiro Ueda, Deputy General Manager responsible for R & D Agricultural Chemicals Div. and Dr. Gozyo Sakata, General Manager of Agricultural Chemicals Research Department of Central Research Institute, Nissan Chemical Ind., Ltd., for their continuing guidance and encouragement.

REFERENCES

1) G. Levitt, H. L. Ploeg, R. C. Weigel & D. J. Fitzgerald: *J. Agric. Food Chem.* **29**, 416 (1981)

2) G. Levitt: "Pesticide Chemistry, Human Welfare and the Environment," ed. by J. Miyamoto & P. C. Kearney, Vol. 1, Pergamon Press, Oxford, pp. 243–250, 1983

3) A. M. Blair & T. D. Martin: *Pestic. Sci.* **22**, 195 (1988)

4) G. Levitt (E. I. du Pont de Nemours & Co.): U. S. US 4169719 (1979)

5) G. Levitt (E. I. du Pont de Nemours & Co.): Eur. Pat. Appl. EP 13480 (1980)

6) "USAN and The USP Dictionary of Drug Names," ed. by M. C. Griffiths, C. A. Fleeger & L. C. Miller, United States Pharmacopeial Convention, Inc., Maryland, U.S.A. 1987

7) "The Pesticide Manual," 8th Ed., ed. by C. R. Worthing & S. B. Walker, The British Crop Protection Council, Thornton Heath, England, 1986

8) F. Suzuki, Y. Iwasawa, T. Sato, T. Ikai & T. Oguti (Nissan Chem. Ind., Ltd.): Eur. Pat. Appl. EP 87780 (1983)

9) S. Yamamoto, T. Sato, T. Ikai, T. Oguti & T. Nawamaki (Nissan Chem. Ind., Ltd.): U.S. US 4668277 (1987)

10) S. Yamamoto, T. Sato, Y. Iwasawa, T. Ikai, K. Suzuki & T. Nawamaki: Abstr. 6th IUPAC Int. Congr. Pestic. Chem., Ottawa, 1B-08, 1986

11) S. Yamamoto, T. Sato, Y. Iwasawa, F. Suzuki, T. Ikai, K. Suzuki & T. Nawamaki: Abstr. 12th Annu. Meet. Pestic. Sci. Jpn., p. 40, 1987

12) K. Suzuki, T. Nawamaki, S. Watanabe & T. Ikai: Proc. 11th Asian-Pacific Weed Sci. Conf., p. 461, 1987

13) K. Suzuki, S. Watanabe, Y. Shirai, T. Endo & H. Hirata: Proc. 12th Asian-Pacific Weed Sci. Conf., p. 141, 1989

14) T. Sato, K. Morimoto & S. Yamamoto: Proc. 53th Symposium on Organic Synthesis, Japan,

pp. 17–20, 1988
15) T. Tanaka: *Yakugaku Zasshi* **91**, 393 (1971) (in Japanese)
16) R. V. Hoffman: *Org. Synth.* **60**, 121 (1981)
17) D. E. Butler & S. M. Alexander: *J. Org. Chem.* **37**, 215 (1972)

要 約

Ethyl 5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl-1-methylpyrazole-4-carboxylate とその関連化合物の選択的除草活性

山本 進，佐藤敏明，岩沢義博，鈴木文夫
猪飼 隆，鈴木宏一，縄巻 勤

Ethyl 5-(4, 6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl-1-methylpyrazole-4-carboxylate (pyrazosulfuron-ethyl, Code No. NC-311, Sirius®) は日産化学工業（株）によって開発された新しい水田用除草剤である．近年，低薬量で効果を示すスルホニルウレア系除草剤が研究され，種々の化合物が開発されてきている．本研究では，ベンゼン環部分のさまざまなヘテロ環への変換を行なった結果，ピラゾール環を導入したピラゾールスルホニルウレア誘導体の中に高い除草活性を見いだした．そのなかで，pyrazosulfuron-ethyl は水田用除草剤として高い活性を示し，圃場試験においては 20～30 g/ha の低薬量でイネに害を及ぼすことなく，多年生雑草を含めた広範囲の雑草に効果を示し，実用性の高い水田用除草剤であることが確認された．これらの化合物の中間体として用いられたピラゾール-5-スルホンアミド誘導体は新規化合物であり，新しく開発した3種類の合成法を用いることにより合成した．