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RELATION BETWEEN STRUCTURE AND HERBICIDAL ACTIVITY OF SUBSTITUTED BENZOTHIADIAZOLES (2,1,3)

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Summary. A large number of substituted benzothiadiazoles (2,1,3) was synthesized. In this report, the herbicidal activities of some halo- and alkyl-substituted benzothiadiazoles (2,1,3) are described. It was found experimentally that at least one of the positions 5 and 6 in the molecule must be unsubstituted. Some di- and tri-substituted derivatives had excellent herbicidal activities, in contrast to tetra-substituted benzothiadiazoles (2,1,3).

Relation entre la structure et l'activité herbicide des (2,1,3) *benzothiadiazoles substitués*

Résumé. Un grand nombre de (2,1,3) benzothiadiazoles substitués ont été synthétisés. Dans cette étude est décrite l'activité herbicide de certains (2,1,3) benzothiadiazoles halo- et alkyl-substitués. Il a été trouvé expérimentalement qu'au moins une des positions 5 et 6 dans la molécule ne doit pas être substituée. Quelques dérivés di- et tri-substitués avaient un excellent pouvoir herbicide, en contraste avec les (2,1,3) benzothiadiazoles tétrasubstitués.

Beziehungen zwischen Struktur und herbizider Wirksamkeit von substituierten Benzothiadiazolen (2,1,3)

Zusammenfassung. Eine grosse Anzahl substituierter Benzothiadiazole-(2,1,3) wurden synthetisiert. In diesem Bericht wird die herbizide Wirksamkeit einiger halo- und alkyl-substituierter Benzothiadiazole-(2,1,3) beschrieben. Es wurde experimentell festgestellt, dass zumindest eine der Positionen 5 und 6 im Molekül unsubstituiert bleiben muss. Im Gegensatz zu tetra-substituierten Derivaten hatten einige der di- und tri-substituierten ausgezeichnete herbizide Wirksamkeit.

INTRODUCTION

After we had found the slight herbicidal activity of benzothiadiazole (2,1,3), many other benzothiadiazoles (2,1,3) were tested. The activities of the halo- and alkyl-substituted benzothiadiazoles (2,1,3), as determined in three herbicidal tests, are described in the present paper.

The synthesis and herbicidal and fungicidal tests of about sixty other benzothiadiazoles (2,1,3) will be reported in 'Recueil des Travaux Chimiques des Pays Bas'.

TEST METHODS

The herbicidal properties were determined in various tests which took into account the three possible ways of uptake of the compounds: via the seeds, via the green parts of the plants (mainly the leaves) or via the roots.

Via the seeds

The inhibition of the germination of seeds of chickweed (*Stellaria media*), millet (*Panicum miliaceum*), wild oat (*Avena fatua*) and garden cress (*Lepidium sativum*) was investigated in a pre-emergence test. In this test 10 ml of a 1% w/v suspension or solution of the compound in acetone was sprayed on a surface area of 0·1 m^2, on which the flats containing a potting soil, sown with the above-mentioned species, had been placed. This rate corresponds to a dose of 10 kg/ha, applied in a spray volume of 1000 litres. Under the experimental conditions in the glasshouse, volatilization of the compounds is negligible, and incorporation of the compounds into the soil was not deemed necessary. Seedling emergence was assessed 14 days after spraying and the results are shown by use of the following symbols: + + no germination; + strong inhibition of germination; ± slight inhibition of germination; − no inhibition.

Via the green parts of the plants

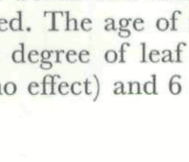
The phytotoxicity was determined by spraying bean (*Phaseolus vulgaris*) tomato (*Lycopersicon esculentum*), oats (*Avena sativa*), chickweed (*Stellaria media*) and beet (*Beta vulgaris*) with a 1% solution of the compound in acetone at a dose corresponding to 10 kg/ha. Acetone applied alone at the same rate did not cause any phytotoxicity. The experiments were carried out with two plants for the beans and tomatoes, five for the beet and about fifty for the oats and chickweed. The age of the plants was from 3 to 4 weeks. Ten days after spraying the degree of leaf damage was assessed and expressed by a figure between 0 (no effect) and 6 (death of the plants).

Via the roots

The effect on the growth of graminaceous plants by watering the roots was determined in the following way: fifty young oat plants 10 cm in height were watered with 25 ml of a 0·1% solution of the compound or with a suspension of the finely ground substance in water corresponding to a dose of 60 kg/ha. After 10 days the leaves were cut off and weighed. This weight was compared with that of the leaves of untreated plants and expressed as a percentage.

RESULTS

The results are summarized in Tables 1, 2 and 3. From Table 1, showing all the halogenated benzothiadiazoles (2,1,3) we see that 4,7-dichlorobenzothiadiazole (2,1,3) has a much higher herbicidal activity than its 4,7-dibromo analogue. This is generally true for all other cases where chlorine was substituted by bromine or fluorine; compare for instance the activities of the compounds k, l, m and n in Table 1. When both positions 5 and 6 in these



(1k)

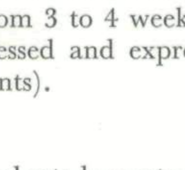


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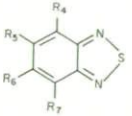
Table 1

Test results of benzothiadiazoles (2,1,3); the parent compound and halogenated compounds

Code					*Inhibition of germination at dose of 10 kg/ha*				*Phytotoxicity at dose of 10 kg/ha*					*Weight of leaves of treated plants as % of weight of control leaves**	*Melting point (°C)*	*Boiling point (°C)*	*Reference*
	R_4	R_5	R_6	R_7	*C*	*PM*	*WO*	*LS*	*B*	*T*	*O*	*C*	*Be*				
a	H	H	H	H		+		+	0	0	0	0	0	25	42–44		2, 3
b	Cl	H	H	H	+	−	+	−	0	0	0	0	0	46	55–58	120–2/12 mm	4 S
c	H	Cl	H	H	−	−	−	−	2	2	0	1	1	113	56–57		4
d	H	F	H	H	−	−		−	0	0	1	1	1	91	30	85–88/13 mm	S
e	Cl	H	H	Cl	++	−	++	+	0	1	0	0	0	52	180–181		5, 3
f	Br	H	H	Br	−	−	−	−	0	0	0	3	2	110	185–187		5
g	Cl	H	Cl	H	++	−	±	++	0	1	0	0	0	28	94–96		3
h	Cl	Cl	H	H	−	−	−	±	1	5	1	2	2	90	141–144		3
i	H	Cl	Cl	H	−	−	−	−	0	0	0	0	0	101	110–112		3
j	Cl	Cl	Cl	H	−	−	−	−	0	0	0	0	0	99	138–142		S
k	Cl	Cl	H	Cl	++	++	++	+	2	2	4	0	3	0	130–131		6†
l	F	Cl	H	Cl	++	−		−	1	0	1	0	0	0	84·0–84·5		S
m	Cl	F	H	Cl	++	+		+	0	1	0	1	1	0	117·5–118·5		S
n	Cl	Br	H	Cl	+	+	++	±	1	1	2	3	2	24	135–137		S
o	Cl	Cl	Cl	Cl	−	−	−	−	1	0	1	1	1	108	156–159		7
p	Br	Cl	Cl	Br	−	−	−	±	1	0	0	1	0	100	200–202		S

* Note: Watering of roots of oats dose 60 kg/ha.

† The m.p.s between 115 and 121° C frequently mentioned in the literature are incorrect.

C = Chickweed, PM = *Panicum miliaceum*, WO = Wild oat, LS = *Lepidium sativum*, B = Bean, T = Tomato, O = Oats, Be = Beet.

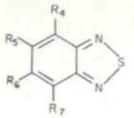
S = Synthesis described.

Inhibition of germination: ++, no germination; +, strong inhibition of germination; ±, slight inhibition; −, no inhibition.

Phytotoxicity: 0 = no effect; 6 = death of the plants.

Table 2

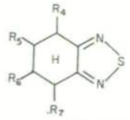
Test results of the alkyl- and alkylchlorobenzothiadazoles (2,1,3)

Code					*Inhibition of germination at dose of 10 kg/ha*				*Phytotoxicity at dose of 10 kg/ha*					*Weight of leaves of treated plants as % of weight of control leaves**	*Melting point (°C)*	*Boiling point (°C)*	*Reference*
	R_4	R_5	R_6	R_7	*C*	*PM*	*WO*	*LS*	*B*	*T*	*O*	*C*	*Be*				
a	CH_3	H	H	H	–	–	–	–	4	2	2	1	2	33		102–104/12 mm	6
b	H	CH_3	H	H	–	–	–	–	4	2	2	2	3	119		106–108/12 mm	3
c	C_2H_5	H	H	H	–	–	–	–	3	3	2	2	2	100		52/0·25 mm	S
d	H	CF_3	H	H	–	–		–	1	1	2	1	1	100	38·5–39·0	86/12 mm	S
e	CH_3	H	H	Cl	++	–	++	–	0	0	0	0	1	21	130–132		8
f	CH_3	Cl	H	H	–	–		–	0	0	1	1	0	14	72–74		9 S
g	CH_3	Cl	H	Cl	++	++	++	+	3	1	3	3	4	10	110–112		6
h	Cl	CH_3	H	Cl	–	–	–	–	2	2	1	3	3	33	139–141		8
i	Cl	Cl	H	CH_3	–	–	–	–	0	3	2	1	2	14	112–115		S
j	C_2H_5	Cl	H	Cl	–	–	–	–	3	4	2	3	4	96	62–63		S
k	CH_3	Cl	Cl	Cl	–	–		–	2	2	1	2	1	100	123–126		S

C = Chickweed, PM = *Panicum miliaceum*, WO = Wild oat, LS = *Lepidium sativum*, B = Bean, T = Tomato, O = Oats, Be = Beet.
S = Synthesis described.
Inhibition of germination: ++, no germination; +, strong inhibition of germination; ±, slight inhibition; –, no inhibition.
Phytotoxicity: 0 = no effect; 6 = death of the plants.
* Note: Watering of roots of oats dose 60 kg/ha.

Table 3

Test results of some tetrahalotetrahydrobenzothiadiazoles (2,1,3)

Code					*Inhibition of germination at dose of 10 kg/ha*				*Phytotoxicity at dose of 10 kg/ha*					*Weight of leaves of treated plants as % of weight of control leaves**	*Melting point (°C)*	*Reference*
	R_4	R_5	R_6	R_7	*C*	*PM*	*WO*	*LS*	*B*	*T*	*O*	*C*	*Be*			
a	Cl	Cl	Cl	Cl	++	±		–	3	3	2	3	4	57	131·0–132·5	5 S
b	Cl	Cl	Cl	Cl	++	–		–	3	2	1	6	2	19	oil	5 S
c	Br	Br	Br	Br	–	–	–	–	0	0	0	0	0	111	152–154	5 S

For footnotes and abbreviations see footnotes to Table 2.

thiadiazoles are halogenated all the herbicidal activity is lost. (Compare the compounds i, j, o and p in Table 1.) The overall conclusion from Table 1 is that 4,5,7-substitution of benzothiadiazole (2,1,3) with chlorine yields the compound with the highest herbicidal activity.

From Table 2 we see that only the chlorine atom at position 4 may be replaced by methyl- (and not by longer alkyl groups). Thus the compound g is the most active compound in this series of Table 2.

The following conclusion may be drawn from Table 3. Only the tetrachlorotetrahydrobenzothiadiazoles (2,1,3) have some herbicidal activity, possibly by generating some dichlorobenzothiadiazole (2,1,3) by splitting off hydrochloric acid. We noticed that the pure compounds dehydrohalogenated spontaneously but slowly.

BIOLOGICAL PROPERTIES

Herbicidally active compounds in this series mainly exhibit activity against germinating seeds and young seedlings. The 4,5,7-trichlorobenzothiadiazole (2,1,3) is the most active compound and can be considered as a potential pre-emergence and early post-emergence herbicide (Daams, 1964).

Table 4

Response of crops to pre-emergence application of 4,5,7-trichlorobenzothiadiazole (2,1,3) on a sandy soil in the glasshouse

	1·5 *kg/ha*	3 *kg/ha*	6 *kg/ha*
Maize (*Zea mays*)	T	T	T
Wheat (*Triticum vulgare*)	T	T	T
Barley (*Hordeum vulgare*)	T	T	T
Oats (*Avena sativa*)	S	S	S
Rice (*Oryza sativa*)	T	T	T
Pea (*Pisum sativum*)	T	T	T
Bean (*Phaseolus vulgaris*)	T	T	T
Soyabean (*Soya hispida*)	T	T	T
Potato (*Solanum tuberosum*)	T	T	S
Sunflower (*Helianthus annuus*)	T	T	S
Cucumber (*Cucumis sativus*)	T	T	S
Groundnut (*Arachis hypogaea*)	T	T	T
Cotton (*Gossypium hirsutum*)	T	T	T

T = tolerant, S = susceptible.

The compounds of this series are mainly absorbed by roots and germinating seeds, and to a slight extent also by leaves and stems. High doses on susceptible plants cause a general growth inhibition, accompanied by browning and other necrotic effects on young leaves and growing points. Swelling of meristematic tissues points to a mode of action connected with the metabolism of actively growing meristems of the plants.

In order to evaluate 4,5,7-trichlorobenzothiadiazole (2,1,3) as a pre- and early post-emergence herbicide we treated a number of crops and weeds with herbicidally effective doses. Pots containing a sandy soil (3% organic matter) in which seeds or tubers of the crops and weeds were planted were sprayed with 4,5,7-trichlorobenzothiadiazole (2,1,3). The compound was applied as an acetone solution at doses of 1·5, 3 and 6 kg/ha by a paint sprayer.

The crops were assessed 3 weeks after application and graded as tolerant (T; no phytotoxic symptoms) or susceptible (S; plants damaged). The results are shown in Table 4, from which it is apparent that nearly all those examined were tolerant, at least to doses of up to 3 kg/ha.

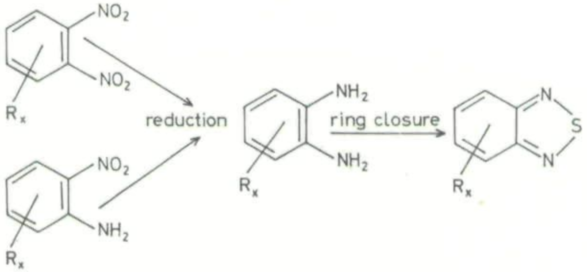
Sixteen weed species were included in the pre-emergence test and it was found that the following important weeds were completely killed by a dose of 1·5 kg/ha: *Poa annua*, *Alopecurus myosuroides*, *Capsella bursa-pastoris*, *Chenopodium album*, *Amaranthus retroflexus*, *Lamium purpureum*, *Galium aparine*, *Polygonum aviculare*, *P. convolvulus*, *Senecio vulgaris*, *Sinapis arvensis*, *Stellaria media*, *Urtica urens* and *Veronica arvensis*. *Avena fatua* was resistant at 1·5 kg/ha but was killed by 3 kg/ha; *Echinochloa crusgalli* tolerated 1·5 and 3 kg/ha but was killed by 6 kg/ha.

Selective effects are probably largely determined by physical factors such as water solubility (2·5 ppm at 20° C), soil humidity, adsorption on soil components, etc.

An example is *Echinochloa crusgalli* which is fairly resistant in normal pre-emergence tests. Treated, however, in an early post-emergence stage (2–3 leaves), it is extremely susceptible to doses of 0·25 kg/ha upwards, especially under humid conditions (see Plate 1). This high activity against *Echinochloa crusgalli* at a low dose seems to be exceptional but at higher rates of 1–3 kg/ha most other weeds are effectively controlled.

SYNTHESIS OF THE COMPOUNDS

For the known compounds we refer to the literature, as indicated in the Tables. Most of the new benzothiadiazoles (2,1,3) mentioned have been synthesized according to the following reaction diagram:



It depends on the properties of the substituents R_x which method for the reduction of the nitro groups must be taken. The ring closure is carried out with thionylchloride and triethylamine or with thionylaniline ($C_6H_5N{=}S{\rightarrow}O$). An example is the synthesis of 5-fluorobenzothiadiazole (2,1,3) (compound 1d)

22·7 g of 3,4-dinitrofluorobenzene (0·122 mol) was dissolved in 100 ml of ethanol, 0·2 g of PtO_2 added and the whole was shaken at atmospheric pressure with hydrogen until 18 litres of hydrogen were taken up. The catalyst was filtered off and the alcohol distilled off at reduced pressure. The residue was dissolved in 150 ml of benzene and 51 g of triethylamine (0·50 mol) was added.

While this was being stirred at room temperature, 30 g of thionylchloride (0·25 mol) was added from a dropping funnel. After being refluxed for 1 hr the mixture was cooled and shaken with 100 ml of water. The benzene layer was separated, filtered through a glass filter, washed again with water, dried over sodium sulphate and distilled.
Boiling point 85–88° C/13 mm. Yield 6·6 g.
Analysis: Calc. for $C_6H_3FN_2S$: C, 46·74; H, 1·96%
Found: C, 46·46; H, 2·50%
The I.R. spectrum (KBr pellet) showed C–F stretching bonds at 1256 and 1197 cm^{-1}.

Table 5
Benzothiadiazoles (2,1,3) synthesized in the same manner as compound 1d

Code	*Starting material*	*Ring closure by:*	*Analysis calc. (%)*	*Analysis found (%)*
1j	2-nitro-3,4,5-trichloroaniline	$C_6H_5N{=}S\rightarrow O$	C, 30·09; H, 0·42; Cl, 44·42; N, 11·70; S, 13·39	C, 30·34; H, 0·71; Cl, 44·10; N, 11·63; S, 13.21
1l	2-nitro-3-fluoro-4,6-dichloroaniline	$SOCl_2+(Et)_3N$	Cl, 31·81; N, 12·56; S, 14·35	Cl, 32·12; N, 11·98; S, 14·09
1m	2-nitro-4-fluoro-3,6-dichloroaniline	$SOCl_2+(Et)_3N$	C, 32·30; H, 0·45; Cl, 31·81; S, 14·35	C, 32·93; H, 1·36; Cl, 31·81; S, 14·08
2c	2-ethyl-6-nitroaniline	$SOCl_2+(Et)_3N$		Analysis see compound 2j
2d	2-nitro-4-trifluoromethylaniline	$SOCl_2+(Et)_3N$	C, 41·17; H, 1·48; N, 13·72; S, 15·71	C, 41·41; H, 2·97; N, 13·71; S, 15·70
2f	2,3-dinitro-6-chlorotoluene	$SOCl_2+(Et)_3N$		Compound known in literature

The following compounds have been synthesized by halogenation of diverse benzothiadiazoles (2,1,3).

Compound 1*b*. Benzothiadiazole (2,1,3) was monochlorinated by the method of Lambert, Ellis & Parry (1965). 218 g of benzothiadiazole (2,1,3) (1·60 mol) was dissolved in 3500 ml of 50% sulphuric acid at 20° C. Within 30 min 70 g of *N*-chlorosuccinimide (0·52 mol) was added and the solution stirred for another 16 hr. The solution was diluted with 3500 ml of water and extracted with chloroform. The chloroform layers were washed with water, dried over sodium sulphate and distilled. The excess of starting material can be used again. Yield 53·2 g of the desired product.

Compound 1*p*. 5·88 g of 4,7-dibromobenzothiadiazole (2,1,3) (0·02 mol) and 1·0 g of $FeCl_3$ were heated at 185–190° C and chlorinated until the first bromine vapours appeared. After cooling, the mixture was taken up in benzene, washed with water and the benzene layer dried over sodium sulphate. Benzene was distilled off and the residue crystallized from benzene/petroleum ether 60–80.
Yield 2·30 g. Melting point 200–202° C.
Total halogen content: Calc. 63·77%, found 62·30%.

Compound 2*j*. 14·3 g of 4-ethylbenzothiadiazole (2,1,3) (compound 2c) was chlorinated at a temperature of 40° C. Chlorine uptake was 11·9 g. The thick oil was dissolved in 100 ml of methanol and 18 ml of a 50% KOH solution was added slowly. After the reaction mixture had been stirred for 3 hr it was poured into 1000 ml of water and the whole extracted with carbon tetrachloride. The carbon tetrachloride layer was dried and distilled *in vacuo*.

B.p. of the product: 115° C/1·2 mm. The compound was recrystallized from petroleum ether 60–80.

Yield 2·9 g.

Analysis: Calc. for $C_8H_6Cl_2N_2S$: C, 41·22; H, 2·60; Cl, 30·42; N, 12·01; S, 13·75%.
Found: C, 41·42; H, 2·72; Cl, 30·36; N, 11·37; S, 13·89%.

Compound 2*k*. 10 g of stannous chloride were added to a solution of 50 g of 4-methyl-5-chlorobenzothiadiazole (2,1,3) (compound 2f) in 350 ml of tetrachloroethane. The mixture was chlorinated at 110° C with excess of chlorine. The stannous chloride was washed out and the remaining solution dried over sodium sulphate. Tetrachloroethane was distilled off at reduced pressure and the residue recrystallized from ethanol. Yield 55 g.

Compounds 3*a and b*. 17·6 g of benzothiadiazole (2,1,3) was chlorinated at 40–50° C. Chlorine uptake was 16·8 g. The thick oil was stirred with ether and the solution chilled at −5° C for 2 days. The crystalline product was filtered off. After recrystallization from ether it had a m.p. of 131·0–132·5° C. Yield 8·2 g (compound 3a). The ether of the mother liquor was distilled off. Yield 22·0 g of an oil (compound 3b).

Analysis: Calc. for $C_6H_4Cl_4N_2S$: C, 25·92; H, 1·46; Cl, 51·02; N, 10·08%.
Found: Compound 3a: C, 26·21; H, 1·55; Cl, 51·12; N, 9·49%.
Compound 3b: C, 25·92; H, 1·61; Cl, 51·25; N, 9·56%.

Compound 3*c*. 81·0 g of benzothiadiazole (2,1,3) was dissolved in 250 ml of carbon tetrachloride and 82 ml of bromine in 160 ml of carbon tetrachloride was added. After 7 days the carbon tetrachloride and excess of bromine was distilled off and the residue recrystallized from acetic acid. Yield 186·0 g of a product with m.p. 152–154° C.

Analysis: Calc. for $C_6H_4Br_4N_2S$: C, 15·81; H, 0·89; Br, 70·12; N, 6·15; S, 7·03%.
Found: C, 15·84; H, 1·00; Br, 68·79; N, 6·05; S, 7·14%.

Compound 1*n*. This compound was formed by diazotization of 4,7-dichloro-5-aminobenzothiadiazole (2,1,3), followed by the Sandmeyer reaction with KBr/CuBr.

Analysis: Calc. for $C_6HCl_2BrN_2S$: C, 25·36; H, 0·35; N, 9·86%.
Found: C, 25·56; H, 0·18; N, 9·55%.

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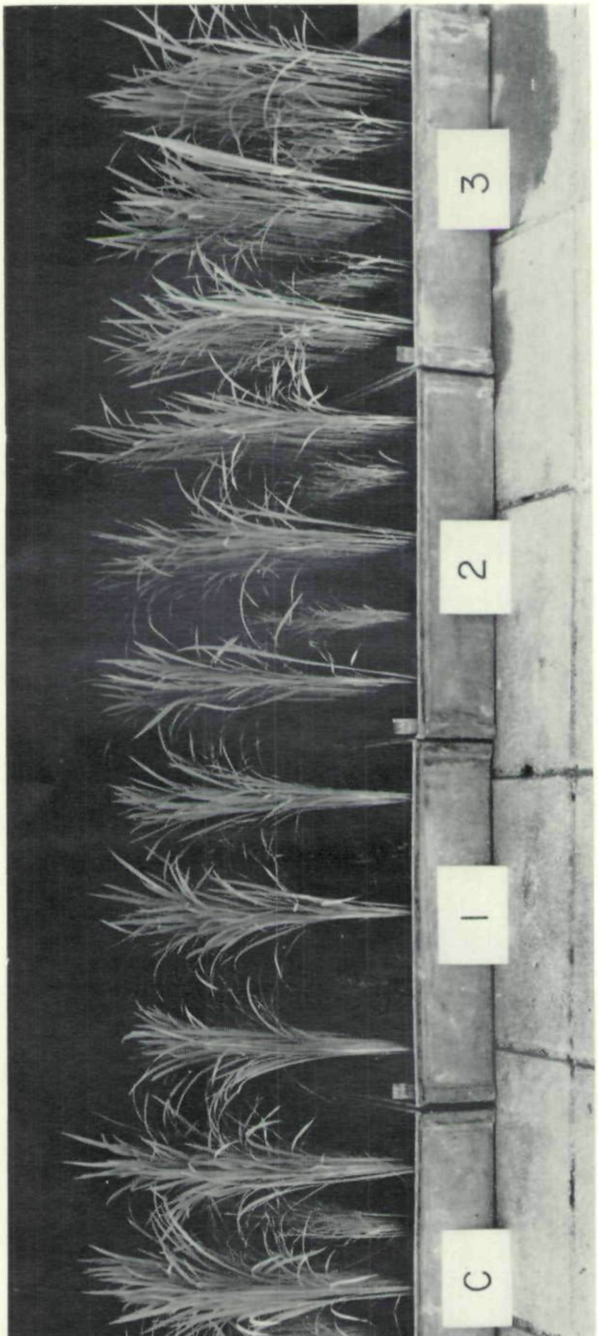

Selective post-emergence activity of 4,5,7-trichlorobenzothiadiazole (2,1,3) (1) on barnyard-grass (*Echinochloa crusgalli*) in transplanted rice. Rate of application: 0·25 kg/ha. Compounds applied in the 2-leaf stage of barnyard grass and 2–3-leaf stage of the rice plants. 4-Methyl-5,7-dichlorobenzothiadiazole (2,1,3) (2) and 4,7-dichlorobenzothiadiazole (2,1,3) (3) do not show any activity at this rate (C = control).