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ORGANIC HERBICIDES. V.*

DERIVATIVES OF 3-MERCAPTO-5-AMINO-1,2,4-THIADIAZOLE

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In this paper we describe the method of preparation and the herbicidal properties of a series of 27 S^3,N^5-disubstituted 3-mercapto-5-amino-1,2,4-thiadiazoles. In this type of compounds we supposed herbicidal effects due to a certain structural similarity with the herbicides of the triazole type. The compounds were prepared by heating S^3-substituted 3-mercapto-5-chloro-1,2,4-thadiazoles (obtained from trichloromethanesulfenyl chloride and corresponding isothiuronium chlorides[1-3]) and amines in alcohol. The yields were above 90%. The prepared compounds are odourless, stable at laboratory conditions, well soluble in common organic solvents, insoluble in water.

For biological testing we made use of Zemánek's method[4] (determination of the inhibition of the growth of wheat and mustard with the tested compounds, untreated plants serving as controls). We found that the majority of compounds displayed the herbicidal effect of the type of growth stimulators (not contact). The measure of these effects is generally lower than necessary for practically utilisable herbicides. The most active of the compounds tested were compounds *IX* and *XV*, *i.e.* those where the substituent R^2 was an isopropylamine group and R^1 and ethylthio- or allylthio group. In contrast to this larger substituents (for example aromatic or heterocyclic) decrease the activity in this type of compounds although these groups by themselves generally do not contribute to increased phytotoxicity. As for the selectivity, the majority of the results indicates a higher effect in mustard, *i.e.* in a representative of large-leaved, dicotyledons.

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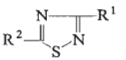
TABLE I

S^3,N^5-Disubstituted 3-Mercapto-5-amino-1,2,4-thiadiazoles and Their Herbicidal Effect on Wheat and Mustard at 50 and 5 p.p.m. Concentration



Compound	R^1 R^2	Composition (mol. weight)	M.p., °C	Calculated/Found				Effect on wheat (mustard)	
				% C	% H	% N	% S	50	5
I	CH_3S CH_3NH	$C_4H_7N_3S_2$ (161·2)	145[a,b]	29·79 29·82	4·37 4·40	26·06 25·83	39·77 39·88	0 (0)	0 (0)
II	CH_3S C_2H_5NH	$C_5H_9N_3S_2$ (175·3)	87[c]	34·26 34·33	5·17 5·24	23·97 24·13	36·59 36·83	0 (0)	0 (0)
III	CH_3S $(CH_3)_2CHNH$	$C_6H_{11}N_3S_2$ (189·3)	61[d]	38·06 38·11	5·86 5·91	22·20 22·40	33·88 34·11	44 (64)	3 (28)
IV	CH_3S C_6H_5NH	$C_9H_9N_3S_2$ (223·3)	157·5[e,k]	48·40 48·38	4·06 3·99	18·82 18·80	28·72 28·57	16 (36)	16 (24)
V	CH_3S c-$C_6H_{11}NH$	$C_9H_{15}N_3S_2$ (229·4)	129[f]	47·12 47·10	6·60 6·66	18·32 18·47	27·96 28·34	28 (63)	0 (36)
VI	CH_3S 4′-morfolino	$C_7H_{11}N_3OS_2$ (217·3)	94·5[b]	38·68 38·85	5·10 5·14	19·34 19·37	29·51 29·83	21 (24)	10 (0)
VII	C_2H_5S CH_3NH	$C_5H_9N_3S_2$ (175·3)	102[a,b]	34·26 34·26	5·17 5·27	23·97 24·12	36·59 36·86	0 (0)	0 (0)
VIII	C_2H_5S C_2H_5NH	$C_6H_{11}N_3S_2$ (189·3)	66·5[g]	38·06 37·98	5·86 5·85	22·20 22·19	33·88 33·98	0 (0)	0 (0)
IX	C_2H_5S $(CH_3)_2CHNH$	$C_7H_{13}N_3S_2$ (203·3)	75·5[h]	41·35 41·30	6·44 6·36	20·67 20·57	31·54 31·73	55 (65)	16 (22)
X	C_2H_5S C_6H_5NH	$C_{10}H_{11}N_3S_2$ (237·3)	163[e]	50·60 50·51	4·67 4·76	17·70 17·57	27·02 27·43	4 (27)	3 (24)
XI	C_2H_5S c-$C_6H_{11}NH$	$C_{10}H_{17}N_3S_2$ (243·4)	85[d]	49·34 49·39	7·04 7·07	17·26 17·16	26·35 26·43	56 (60)	0 (10)

TABLE I
(*Continued*)

Compound	R^1 R^2	Composition (mol. weight)	M.p., °C	Calculated/Found				Effect on wheat (mustard)	
				% C	% H	% N	% S	50	5
XII	C_2H_5S 4′-morfolino	$C_8H_{13}N_3OS_2$ (231·3)	70[d]	41·53 41·65	5·66 5·78	18·16 18·18	27·72 27·69	39 (39)	8 (0)
XIII	$CH_2{=}CHCH_2S$ CH_3NH	$C_6H_6N_3S_2$ (184·3)	68[h]	39·11 39·19	3·28 3·34	22·81 23·00	34·80 34·94	0 (0)	0 (0)
XIV	$CH_2{=}CHCH_2S$ C_2H_5NH	$C_7H_8N_3S_2$ (198·3)	103[b]	42·40 42·51	4·07 4·16	21·19 21·09	32·34 32·43	0 (0)	0 (0)
XV	$CH_2{=}CHCH_2S$ $(CH_3)_2CHNH$	$C_8H_{10}N_3S_2$ (212·3)	75[h]	45·25 45·18	4·75 4·77	19·79 19·87	30·20 30·41	60 (83)	14 (44)
XVI	$CH_2{=}CHCH_2S$ C_6H_5NH	$C_{11}H_{11}N_3S_2$ (249·3)	152[e]	52·98 53·10	4·47 4·48	16·85 17·01	25·72 25·61	9 (18)	9 (12)
XVII	$CH_2{=}CHCH_2S$ c-$C_6H_{11}NH$	$C_{11}H_{17}N_3S_2$ (255·4)	76[f]	51·73 51·75	6·71 6·80	16·45 16·35	25·11 25·02	25 (48)	5 (43)
XVIII	$CH_2{=}CHCH_2S$ 4′-morfolino	$C_9H_{13}N_3OS_2$ (243·3)	45[d]	44·42 44·48	5·38 5·38	17·27 17·06	26·35 26·63	50 (64)	5 (25)
XIX	$C_6H_5CH_2S$ CH_3NH	$C_{10}H_{11}N_3S_2$ (237·3)	140[a,b]	50·60 50·64	4·67 4·80	17·70 17·76	27·02 27·33	0 (0)	0 (0)
XX	$C_6H_5CH_2S$ C_2H_5NH	$C_{11}H_{13}N_3S_2$ (251·4)	86·5[f]	52·55 52·78	5·21 5·09	16·72 16·88	25·51 25·48	50 (26)	21 (22)
XXI	$C_6H_5CH_2S$ $(CH_3)_2CHNH$	$C_{12}H_{15}N_3S_2$ (265·4)	91[d]	54·30 54·40	5·70 5·81	15·83 15·69	24·16 24·41	21 (26)	18 (13)
XXII	$C_6H_5CH_2S$ n-C_4H_9NH	$C_{13}H_{17}N_3S_2$ (281·4)	[j]	55·48 55·54	6·09 5·99	14·93 15·11	22·79 23·02	50 (50)	0 (20)
XXIII	$C_6H_5CH_2S$ $CH_2{=}CHCH_2NH$	$C_{12}H_{13}N_3S_2$ (263·4)	96·5[f]	54·72 54·68	4·97 5·13	15·95 16·02	24·35 24·18	23 (15)	20 (0)
XXIV	$C_6H_5CH_2S$ C_6H_5NH	$C_{15}H_{13}N_3S_2$ (299·4)	152·5[i,k]	60·17 60·16	4·38 4·50	14·03 13·89	21·42 21·63	6 (12)	4 (0)

TABLE I
(*Continued*)

Compound	R^1 R^2	Composition (mol. weight)	M.p., °C	Calculated/Found				Effect on wheat (mustard)	
				%C	%H	%N	%S	50	5
XXV	$C_6H_5CH_2S$ c-$C_6H_{11}NH$	$C_{15}H_{19}N_3S_2$ (305·4)	132[f]	58·98 59·07	6·27 6·35	13·76 13·59	20·99 21·25	3 (0)	0 (0)
XXVI	$C_6H_5CH_2S$ 4′-morfolino	$C_{13}H_{15}N_3OS_2$ (293·4)	81[d]	53·21 53·17	5·15 5·06	14·32 14·26	21·86 22·07	11 (8)	3 (0)
XXVII	$C_6H_5.CH_2S$ 1′-piperidino	$C_{14}H_{17}N_3S_2$ (291·4)	49·5[d]	57·69 57·76	5·88 6·02	14·42 14·31	22·00 22·32	0 (0)	0 (0)

[a] M.p. agrees with literature data[1]. Solvents used for crystallisation: [b] methanol, [c] 50% aqueous methanol, [d] n-hexane, [e] n-heptane–benzene (5 : 1), [f] n-heptane, [g] 60% aqueous methanol, [h] light petroleum b.p. 40–60°C, [i] n-heptane–benzene (4 : 1), [j] b.p. 14°C/0·01 Torr, n_D^{20} 1·6069, [k] literature[5] gives m.p. of compound *IV* 154–155°C, and compound *XXIV* 150–151°C.

EXPERIMENTAL

Melting and boiling points are corrected. Samples for analysis were dried at 20°C and 0·1 Torr for 24 hours over phosphorus pentoxide.

Starting Compounds

For condensations 3-methylthio-5-chloro-1,2,4-thiadiazole was used of b.p. 95°C/15 Torr and m.p. 30°C, further 3-ethylthio-5-chloro-1,2,4-thiadiazole of b.p. 110°C/10 Torr and n_D^{20} 1·5828, 3-allylthio-5-chloro-1,2,4-thiadiazole of b.p. 115°C/15 Torr, and 3-benzylthio-5-chloro-1,2,4-thiadiazole of b.p. 125°C/0·5 Torr and m.p. 50°C. They were prepared according to literature (ref.[1–3]).

Substituted 3-Mercapto-5-amino-1,2,4-thiadiazoles

To a solution of 0·01 mol of 3-alkyl-, 3-alkenyl-, or 3-arylalkylthio-5-chloro-1,2,4-thiadiazole in 20 ml of methanol 20 ml of a methanolic solution of the corresponding amine (0·025 mol) were added and the mixture was refluxed on a water bath. Methanol and the excess amine were then distilled off and the residue was extracted three times with 25 ml portions of ice-cold water, in order to eliminate the amine hydrochloride. After filtering off with suction and drying the water-insoluble residue was crystallised from a suitable solvent; in the case of the oily compound *XXII* it was distilled *in vacuo*. The list of compounds prepared and their properties are given in Table I.

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ORGANISCHE HERBIZIDE VI.*

3,5-DISUBSTITUIERTE 1,2,4-THIADIAZOLE

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In der vorliegenden Mitteilung werden die Darstellungsweise und die physikalisch-chemischen und herbiziden Eigenschaften einer Reihe von 53 neuen 3-alkyl-, 3-arylalkyl- und 3-aryl-5-substituierten 1,2,4-Thiadiazolen beschrieben. Die Bereitung dieser Verbindungen erfolgte mit hohen Ausbeuten (85–95%) durch Reaktion der entsprechenden 3-substituierten 5-Chlor-1,2,4-thiadiazolen[1], die aus Trichlormethansulfenylchlorid und Amidinhydrochloriden gewonnen wurden, mit Aminen unter Erhitzen in Alkohol. Diesen Verbindungen wurde größere Aufmerksamkeit geschenkt, nachdem festgestellt wurde, daß die von uns bereits früher bereiteten und getesteten Stoffe vom Typ der 3-Alkylthio-, 3-Alkenylthio- und 3-Arylalkylthio-5-subst.amino-1,2,4-thiadiazole[2] herbizid wirksam sind. Die Mehrzahl der bereiteten Verbindungen ist kristallin. Unter normalen Bedingungen sind die Substanzen beständig und in organischen Lösungsmitteln löslich, hingegen in Wasser unlöslich.

Die biologische Testung wurde nach der Methode von Zemánek[3] vorgenommen (Bestimmung der durch die Verbindung bewirkten Wachstumshemmung von Weizen- und Senfpflanzen unter Bezug auf die unbehandelten Kontrollpflanzen). Aus den erhaltenen Resultaten lassen sich folgende Schlußfolgerungen ziehen: Der untersuchte Verbindungstyp besitzt herbizide Eigenschaften vom Typus der Wachstumsstimulatoren sowohl gegenüber Vertretern von ein- als auch zweikeimblättrigen Pflanzen. Im Vergleich mit dem ähnlichen Verbindungstyp, bei dem R^1 eine Alkylthio- oder Arylalkylthiogruppe ist[2], weist der jetzt beschriebene Typ, bei dem R^1 eine Alkyl-, Arylalkyl- bzw. Arylgruppe ist, eine durchweg höhere herbizide Wirksamkeit auf. Die

* V. Mitteilung: diese Zeitschrift *36*, 4087 (1971).