Synthesis and pesticidal activity of *N*-arylcarbamoyl--5,6-dihydro-1,4-dithiin-2,3-dicarboximides

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The synthesis and the i.r. spectra of *N*-arylcarbamoyl-5,6-dihydro-1,4-dithiin-2,3-dicarboximides are described. The fungicidal and herbicidal activities of these compounds were found to be very low in comparison to those of the used standards.

Описывается синтез и ИК спектры *N*-арилкарбамоил-5,6-дигидро-1,4-дитиин-2,3-дикарбоксимидов. У этих соединений обнаружено очень слабое фунгицидное и гербицидное действие по сравнению с используемыми стандартами.

We described earlier the use of 5,6-dihydro-1,4-dithiin-2,3-dicarboximide at the synthesis of *O*,*O*-dialkyl *S*-(5,6-dihydro-1,4-dithiin-2,3-dicarboximidomethyl) thio- and dithiophosphates which exhibited acaricidal and fungicidal activities [1]. In the present work we synthesized *N*-arylcarbamoyl-5,6-dihydro-1,4-dithiin-2,3-dicarboximides *I—XVIII* (Table 1) by the reaction of 5,6-dihydro-1,4-dithiin-2,3-dicarboximide with aryl isocyanate in toluene at increased temperature using triethylamine as an advantageous catalyst.

All the prepared compounds showed an absorption band of medium intensity at about 1700 cm^{-1} which could be attributed to stretching vibration of the carbonyl group in the side chain. In the region of 1750 and 1800—1780 cm^{-1} more intensive absorption bands were observed. These bands belonged to symmetrical and asymmetrical stretching vibrations of C=O in the cyclic dicarbonyl system. The absorption band at 1880—1780 cm^{-1} was generally split with all compounds probably due to further vibrational couplings in the whole tricarbonyl system. In the region of 3400—3300 cm^{-1} weaker absorption bands attributed to the stretching N—H vibration were observed. The medium absorption band at 1570—1550 cm^{-1} could be ascribed to the stretching vibration of the double C=C bond in the heterocyclic ring.

The fungicidal and herbicidal activities of the synthesized compounds were found to be very low, therefore they were not investigated further in precise tests.

Experimental

Physical constants and data of elemental analyses of the synthesized compounds are presented in Table 1.

The i.r. spectra of the synthesized compounds were measured on a Zeiss UR 20 spectrophotometer in paraffin oil suspensions (4000—700 cm^{-1}) and in chloroform solutions (1800—1600 cm^{-1}). In the latter case cells of 0.25 and 0.5 mm thickness were used. The apparatus was calibrated with polystyrene foil.

N-Arylcarbamoyl-5,6-dihydro-1,4-dithiin-2,3-dicarboximides (I—XVIII)

To 5,6-dihydro-1,4-dithiin-2,3-dicarboximide (0.05 mol) dissolved in anhydrous toluene (80 ml) aryl isocyanate (0.05 mol) and then triethylamine (0.1 ml) were added under stirring. The reaction mixture was stirred for 4 h at boiling. After cooling, the formed product was filtered and purified by crystallization from acetonitrile.

N-Methyl-5,6-dihydro-1,4-dithiin-2,3-dicarboximide (XIX)

To 5,6-dihydro-1,4-dithiin-2,3-dicarboximide (0.05 mol) dissolved in anhydrous toluene (100 ml), triethylamine (0.1 ml) and then methyl isocyanate (0.055 mol) were added under stirring which was continued for 3 h at 20°C and for the same time at 60°C. After cooling the formed product was filtered and purified by crystallization. Yield 76.2%, m.p. 212°C (decomposition).

For $C_8H_8N_2O_3S_2$ (244.27) calculated: 11.47% N, 26.25% S; found: 11.72% N, 26.40% S.

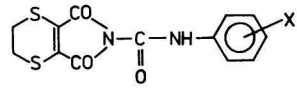
Pesticidal activity

Fungicidal activity of the synthesized compounds was determined by *in vivo* and *in vitro* methods. Inherent activity was followed on spores of *Sclerotinia fructicola* (WINT.), *Aspergillus niger* TIEGH, *Fusarium nivale* (FR.) CES., *Alternaria sp.*, and *Stemphylium sarcinoformae* (CAV.) WITHSHIRE by the method after Sharvell. Antipowdery mildew activity was followed on living plants of spring barley, sort Dunajský trh (*Erysiphe graminis* DC.), on cucumbers, sort Znojemské (*Erysiphe cichoriacearum* DC.), and on tomatoes (*Phytophthora infestans* De BY).

Herbicidal activity was determined by the method of preemergence (into the soil) and postemergence (to the leaf) application using the following test objects: *Avena sativa* L., *Polygonum persicaria, Fagopyrum sagitatum* L., and *Sinapis alba* L.

Table 1

Characterization of the synthesized compounds



Compound	X	Formula	*M*	Calculated/found % N	% S	% X	Yield %	M.p. °C
I	H	$C_{13}H_{10}N_2O_3S_2$	306.34	9.14 9.37	20.93 21.05		91.4	125—128
II	4-Br	$C_{13}H_9BrN_2O_3S_2$	385.25	7.27 7.76	16.64 16.82	20.74 20.96	92.1	218—220
III	4-Cl	$C_{13}H_9ClN_2O_3S_2$	340.79	8.22 8.32	18.82 19.11	10.40 10.51	88.4	155—157
IV	4-F	$C_{13}H_9FN_2O_3S_2$	324.34	8.64 9.01	19.77 19.58	5.86 5.91	94.6	168—170
V	4-I	$C_{13}H_9IN_2O_3S_2$	432.25	6.48 6.84	14.83 14.95	29.36 29.41	88.1	181—182
VI	4-CH_3	$C_{14}H_{12}N_2O_3S_2$	320.36	8.74 9.01	20.02 19.88	—	92.3	208—210
VII	4-OCH_3	$C_{14}H_{12}N_2O_4S_2$	336.36	8.33 8.11	19.06 19.00	—	88.9	170—173
VIII	4-NO_2	$C_{13}H_9N_3O_5S_2$	351.34	11.96 12.05	18.25 18.32	—	81.2	228—230
IX	3-Cl	$C_{13}H_9ClN_2O_3S_2$	340.79	8.22 8.12	18.82 18.60	10.40 10.61	96.1	147—149
X	3-CH_3	$C_{14}H_{12}N_2O_3S_2$	320.36	8.74 8.61	20.02 19.91	—	94.4	154—155
XI	3-OCH_3	$C_{14}H_{12}N_2O_3S_2$	336.36	8.33 8.66	19.06 19.25	—	85.4	176—177
XII	3-CF_3	$C_{14}H_9F_3N_2O_3S_2$	374.35	7.48 7.46	17.13 17.10	15.23 15.11	87.6	219—220
XIII	3-NO_2	$C_{13}H_9N_2O_3S_2$	351.34	11.96 11.88	18.25 18.61	—	86.1	218—220
XIV	3,4-Cl_2	$C_{13}H_8Cl_2N_2O_3S_2$	375.24	7.46 7.61	17.08 16.98	18.89 19.12	89.6	179—181
XV	3-Cl-4-CH_3	$C_{14}H_{11}ClN_2O_3S_2$	354.89	7.89 7.95	18.07 18.00	10.01 10.10	88.4	178—181
XVI	4-Cl-3-CF_3	$C_{14}H_8ClF_3N_2O_3S_2$	408.80	6.85 7.04	15.68 16.00	—	79.2	188—191
XVII	4-Cl-3-NO_2	$C_{13}H_8ClN_3O_5S_2$	385.79	10.89 11.03	16.62 16.90	99.22 9.41	68.9	205—208
XVIII	2,4,5-Cl_3	$C_{14}H_7Cl_3N_2O_3S_2$	409.69	6.84 7.07	15.65 15.48	25.96 26.11	84.6	210—212

The methods for the determination of fungicidal and herbicidal activities on the individual test objects were published earlier [2, 3].

References

1. Konečný, V., Hrnčiar, P., and Gregáň, F., *Chem. Zvesti* ***27,*** 411 (1973).
2. Demečko, J. and Konečný, V., *Agrochémia* (Bratislava) ***10,*** 5 (1970).
3. Furdík, M., Konečný, V., Šály, A., and Truchlik, Š., *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* ***XII,*** 45 (1968).

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