

5-Acyloxy-3,4-dichloro-5H-furan-2-ones

*A. KRUTOŠÍKOVÁ, *A. KOREŇOVÁ, *J. KOVÁČ, and ^bV. KONEČNÝ

^aDepartment of Organic Chemistry, Slovak Technical University,
CS-812 37 Bratislava

^bResearch Institute of Chemical Technology,
CS-831 06 Bratislava

Received 29 May 1985

Paper published on the occasion of the 45th anniversary of the foundation of the Department of Organic Chemistry, Slovak Technical University, Bratislava

A synthesis of novel fungicidally active 5-acyloxy-3,4-dichloro-5H-furan-2-ones prepared by the reaction of chlorides or mixed anhydrides of 5-aryl-2-furancarboxylic and 3-arylpropenoic acids with 5-hydroxy-3,4-dichloro-5H-furan-2-one is described.

Описан синтез новых фунгицидно активных 5-ацилокси-3,4-дихлор-5H-фуран-2-онов посредством реакции хлоридов или смешанных ангидридов 5-арил-2-фуранкарбоновой и 3-арилакриловой кислот с 5-гидрокси-3,4-дихлор-5H-фуран-2-оном.

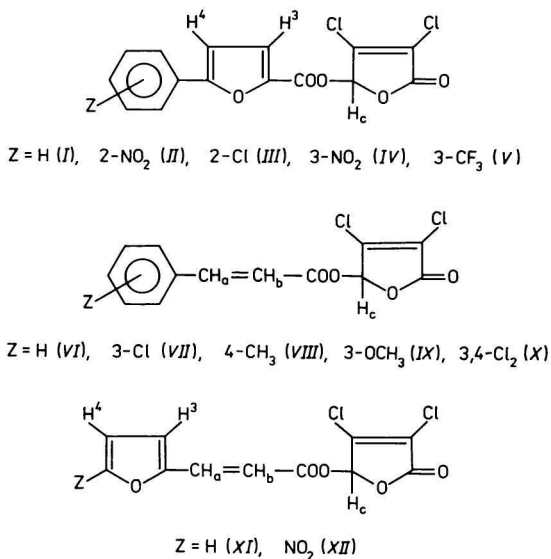
In the area of novel chemical means against diseases of plants a discovery of system fungicides signifies a great progress. It is known [1] that 3,4-disubstituted 5-acyloxy-5H-furan-2-ones possess good fungicidal properties for the inhibition of the growth of phytopathogenic fungi as *Fusarium nivele*, *Tilletia caries*, *Sclerotinia fructicola*, *Botrytis cinerea*.

These types as well as their analogues [2, 3] can be used for application as seed disinfectants mainly for the protection of the rye against fusariosis and of the wheat against its sticky mildew. Also other 3,4-disubstituted 5-alkoxy-5H-furan-2-ones [4—7] and their sulfur analogues [8] are suitable for the suppression of phytopathogenic fungi.

This work deals with the synthesis of new 5-acyloxy-3,4-dichloro-5H-furan-2-ones and the study of their fungicidal properties. Compounds I—XII (Scheme 1, Table 1) were prepared by reaction of chlorides or mixed anhydrides of 5-aryl-2-furancarboxylic and 3-arylpropenoic acids with 5-hydroxy-3,4-dichloro-5H-furan-2-one (mucochloric acid).

Structure of the synthesized compounds was proved by ¹H NMR spectra (Table 2). The ¹H NMR spectra of all compounds have a signal (singlet) of proton on C-5 of 5-hydroxy-3,4-dichloro-5H-furan-2-one. The spectra of I—V, XI, XII showed the doublets of protons C-3—H and C-4—H of the furan ring with an

interaction constant $J_{3,4} = 3.4$ Hz. From the interaction constant $J_{A,B} = 16$ Hz of VI—XII it can be concluded that a double bond of propenyl group has an *E*-configuration.



Scheme 1

By testing the compounds for relative fungicidal activity (Table 3) it was found that the compounds IV, VI, IX—XII were in tests against *T. caries* good active, but none of them was so active as the used standard Vitavax. In tests against *F. avenaceum* the compound I reached the activity of the used standard captan, however, also the compounds IV, VII—IX, XI, and XII showed a relatively good activity. Against *B. cinerea* the compounds I—IV and XI were a little less active than the standard captan. The compound XI was against *A. alternata* active as the used standard captan, nevertheless further compounds I, V, VII—IX, and XII were a little less active. Compounds I and XI were as active as the used standard Dithane M-45 against *P. infestans*, also the compounds IV, VI—X, and XI exhibited interesting activity.

The compounds I and XI were advanced to further screening.

Experimental

The ^1H NMR spectra were recorded with a Tesla BS 487 C apparatus operating at 80 MHz. Tetramethylsilane was used as internal reference.

Table 1
Characterization of the prepared compounds

Compound	Formula	M_r	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$				Yield %	M.p. °C
			C	H	Cl	N		
<i>I</i>	$\text{C}_{15}\text{H}_8\text{Cl}_2\text{O}_4$	323.1	55.75	2.49	2.94		78	89—90
			55.65	2.39	21.78			
<i>II</i>	$\text{C}_{15}\text{H}_7\text{Cl}_2\text{NO}_6$	368.1	48.94	1.92	19.26	3.80	75	160—162
			48.92	1.90	19.20	3.62		
<i>III</i>	$\text{C}_{15}\text{H}_7\text{Cl}_3\text{O}_4$	357.6	50.38	1.97	29.74		70	94—95
			50.30	1.90	29.72			
<i>IV</i>	$\text{C}_{15}\text{H}_7\text{Cl}_2\text{NO}_6$	368.1	48.94	1.92	19.26	3.80	74	182—183
			48.78	1.90	19.08	3.78		
<i>V</i>	$\text{C}_{16}\text{H}_7\text{F}_3\text{Cl}_2\text{O}_4$	391.1	49.13	1.80	18.12		80	139—141
			49.10	1.82	18.04			
<i>VI</i>	$\text{C}_{13}\text{H}_8\text{Cl}_2\text{O}_3$	283.1	55.15	2.84	25.04		75	93—94
			55.10	2.72	25.20			
<i>VII</i>	$\text{C}_{13}\text{H}_7\text{Cl}_3\text{O}_4$	315.6	49.17	2.22	33.49		65	92—95
			49.07	2.08	33.39			
<i>VIII</i>	$\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{O}_2$	297.6	56.59	3.39	23.86		65	85—86
			56.49	3.29	23.76			
<i>IX</i>	$\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{O}_4$	313.1	53.70	3.22	22.64		68	85—87
			53.80	3.20	22.60			
<i>X</i>	$\text{C}_{13}\text{H}_6\text{Cl}_4\text{O}_3$	352.0	44.35	1.72	40.28		70	145—148
			44.32	1.70	40.26			
<i>XI</i>	$\text{C}_{11}\text{H}_6\text{Cl}_2\text{O}_4$	273.1	48.38	2.21	25.96		60	100—101.5
			48.40	2.28	25.92			
<i>XII</i>	$\text{C}_{11}\text{H}_5\text{Cl}_2\text{NO}_6$	218.1	41.54	1.58	22.29	4.40	60	135—138
			41.38	1.70	22.09	4.32		

Table 2

¹H NMR spectral data (δ /ppm) of the synthesized compounds

Compound	H-3	H-4	$J_{3,4}$	H _a	H _b	H _c	H _{arom}	Others
I	7.64	7.40	3.6	—	—	7.33	7.75—8.37	
II	7.63	7.04	3.6	—	—	7.33	7.75—8.12	
III	7.63	7.34	3.6	—	—	7.36	7.40—8.10	
IV	7.66	7.44	3.6	—	—	7.38	7.80—8.60	
V	7.64	7.37	3.8	—	—	7.37	7.75—8.37	
VI	—	—	—	7.92	6.63	7.24	7.37—8.87	
VII	—	—	—	7.92	6.75	7.27	7.37—7.78	
VIII	—	—	—	7.87	6.57	7.23	7.26—7.62	2.37 (CH ₃)
IX	—	—	—	7.90	6.66	7.26	6.93—7.50	3.85 (OCH ₃)
X	—	—	—	7.90	6.67	7.24	7.62—8.15	
XI	7.64	7.30	3.8	7.90	6.65	7.23	—	
XII	7.64	7.35	4.0	7.80	6.72	7.26	—	

 $J_{A,B} = 16$ Hz

Table 3

Fungicidal activity of the synthesized compounds

Compound	<i>Tilletia caries</i>	<i>Fusarium avenaceum</i>	<i>Botrytis cinerea</i>	<i>Alternaria alternata</i>	<i>Phytophthora infestans</i>
I	0	4	3	3	4
II	1	0	3	0	0
III	0	0	3	0	0
IV	3	3	3	0	3
V	0	0	3	3	0
VI	3	0	0	0	3
VII	0	3	0	3	3
VIII	0	3	0	3	3
IX	3	3	0	3	3
X	3	0	0	0	3
XI	3	3	3	4	4
XII	3	3	0	3	3
Vitavax	4	—	—	—	—
captan	—	4	4	4	—
Dithane M-45	—	—	—	—	4

Fungicidal activity of the prepared compounds was examined by the method *in vitro* on spores of fungus: *Tilletia caries*, *Botrytis cinerea*, *Alternaria alternata*, and *Phytophthora infestans* according to previously published methods [9]. The evaluation of the activity was carried out according to the scale (a/%, 0–0, 1–25, 2–50, 3–75, and 4–100) using standards: Vitavax (2,3-dihydro-5-carboxanilide-6-methyl-1,4-oxathiin), captan (cis-N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide), and Dithane M-45 (a mixture of manganese(II) and zinc(II) 1,2-ethanediy-bis(carbamodithioates)).

3,4-Dichloro-5-(5-aryl-2-furoyloxy)-5H-furan-2-ones (I—V)

3,4-Dichloro-5-hydroxy-5H-furan-2-one (0.01 mol) and chloride of 5-aryl-2-furan-carboxylic acid [10—12] (0.01 mol) in benzene (15 cm³) were refluxed until the evolution of HCl was ceased. Reaction mixture was cooled and the residue was filtered off and crystallized from benzene or diluted ethanol.

3,4-Dichloro-5-(3-arylpropenoxy)-5H-furan-2-ones (VI—XII)

3,4-Dichloro-5-hydroxy-5H-furan-2-one (0.01 mol) and mixed anhydride of trifluoroacetic and 3-arylpropenoic acids in toluene (10 cm³) were mixed for 2 h at room temperature. The solvent was distilled off *in vacuo* and the residue was crystallized from benzene or methanol.

References

1. Beška, E., Rapoš, P., and Fandlová, M., *Czechoslov.* 166140 (1976); *Chem. Abstr.* 87, 17295u (1977).
2. Mowry, D. T., *J. Amer. Chem. Soc.* 72, 2535 (1950).
3. Gilbert, E. E. and Rumanowski, E. J., *U.S.* 2786798 (1957); *Chem. Abstr.* 51, 9996i (1957).
4. Beška, E. and Rapoš, P., *Czechoslov.* 149048 (1973); *Chem. Abstr.* 80, 36982u (1974).
5. Beška, E., Rapoš, P., and Fandlová, M., *Czechoslov.* 148592 (1973); *Chem. Abstr.* 80, 14835g (1974).
6. Beška, E., Rapoš, P., and Demečko, J., *Czechoslov.* 170448 (1977); *Chem. Abstr.* 88, 169946r (1978).
7. Rapoš, P., Winternitz, P., Sohler, E., and Beška, E., *Czechoslov.* 138602 (1970); *Chem. Abstr.* 76, 14320k (1972).
8. Rapoš, P., Winternitz, P., Beška, E., and Sohler, E., *Czechoslov.* 138821 (1970); *Chem. Abstr.* 76, 34093s (1972).
9. Konečný, V., Kováč, Š., and Varkonda, Š., *Chem. Zvesti* 38, 239 (1984).
10. Krutošíková, A., Kováč, J., Rentka, J., and Čakrt, M., *Collect. Czechoslov. Chem. Commun.* 39, 767 (1974).
11. Krutošíková, A., Kováč, J., and Sýkora, V., *Collect. Czechoslov. Chem. Commun.* 39, 1892 (1974).
12. Krutošíková, A. and Kováč, J., *Collect. Czechoslov. Chem. Commun.* 41, 2577 (1976).

Translated by A. Krutošíková