



Table 1. Characterization of the Prepared Compounds

Compound	R <sup>1</sup>	R <sup>2</sup>	Formula M <sub>r</sub>	w <sub>i</sub> (calc.)/% w <sub>i</sub> (found)/%			Yield %	M.p. °C	M <sup>+</sup> m/z
				S	N	P			
I	H	C(S)OCH <sub>3</sub>	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> S <sub>2</sub> 232.3	27.61 27.30	— —	— —	62	108	232
II	H	C(S)C <sub>2</sub> H <sub>5</sub>	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> S <sub>2</sub> 246.3	26.30 26.40	— —	— —	70	112	246
III	H	C(S)OC <sub>3</sub> H <sub>7</sub>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub> 260.3	24.63 24.50	— —	— —	61	111	260
IV	H	C(S)OC <sub>4</sub> H <sub>9</sub> -i	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> S <sub>2</sub> 274.3	23.37 23.61	— —	— —	80	94	274
V	H	C(S)OCH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> S <sub>3</sub> 258.3	24.82 25.02	— —	— —	74	172	258
VI	H	C(S)N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>11</sub> NO <sub>3</sub> S <sub>2</sub> 245.3	26.14 26.12	5.71 5.80	— —	79	156	245
VII	ClCH <sub>2</sub> CO	C(S)N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>11</sub> H <sub>12</sub> ClNO <sub>4</sub> S <sub>2</sub> 321.8	19.93 20.26	4.35 <sup>a</sup> 4.50	— —	69	182	322
VIII	CH <sub>3</sub>	C(S)N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>10</sub> H <sub>13</sub> NO <sub>3</sub> S <sub>2</sub> 259.3	24.72 25.06	5.40 5.50	— —	71	188	259
IX	H	C(S)N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>11</sub> H <sub>15</sub> NO <sub>3</sub> S <sub>2</sub> 273.4	23.45 23.09	5.12 5.08	— —	69	116	273
X	H	C(S)N(C <sub>2</sub> H <sub>5</sub> )(C <sub>4</sub> H <sub>9</sub> )	C <sub>16</sub> H <sub>19</sub> NO <sub>3</sub> S <sub>2</sub> 301.4	21.28 21.49	4.64 4.70	— —	81	104	301
XI	H	C(S)piperidinyI	C <sub>15</sub> H <sub>15</sub> NO <sub>3</sub> S <sub>2</sub> 285.4	22.47 22.61	4.90 5.21	— —	79	200 decomp.	285
XII	H	C(S)morpholinyl	C <sub>14</sub> H <sub>13</sub> NO <sub>4</sub> S <sub>2</sub> 287.4	22.31 22.60	4.90 4.80	— —	74	190	287
XIII	H	P(S)(OCH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>11</sub> O <sub>5</sub> PS <sub>2</sub> 282.3	22.72 22.48	— —	10.97 10.70	68	165	282
XIV	H	P(S)(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>10</sub> H <sub>15</sub> O <sub>5</sub> PS <sub>2</sub> 310.5	20.66 20.86	— —	9.98 10.20	71	109	310
XV	CH <sub>3</sub>	P(S)(OCH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>13</sub> O <sub>5</sub> PS <sub>2</sub> 296.3	21.64 21.39	— —	10.45 10.38	67	visc. liq.	296
XVI	CH <sub>3</sub>	P(S)(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>11</sub> H <sub>17</sub> O <sub>5</sub> PS <sub>2</sub> 324.3	19.76 20.07	— —	9.55 9.78	76	visc. liq.	324
XVII	H	P(S)(OC <sub>5</sub> H <sub>11</sub> ) <sub>2</sub>	C <sub>16</sub> H <sub>27</sub> O <sub>5</sub> PS <sub>2</sub> 394.5	16.26 16.41	— —	7.85 8.05	84	47	394
XVIII	H	P(S)(OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> O <sub>5</sub> PS <sub>2</sub> 406.4	15.72 16.08	— —	7.62 7.78	80	124	406
XIX	H	P(S)(C <sub>2</sub> H <sub>5</sub> )(OC <sub>2</sub> H <sub>5</sub> )	C <sub>10</sub> H <sub>15</sub> O <sub>4</sub> PS <sub>2</sub> 254.3	21.78 22.08	— —	10.52 10.68	69	110	294
XX	H	P(S)(SC <sub>2</sub> H <sub>5</sub> )(OC <sub>2</sub> H <sub>5</sub> )	C <sub>10</sub> H <sub>15</sub> O <sub>5</sub> PS <sub>2</sub> 310.3	20.68 21.04	— —	9.49 9.79	69	149	310
XXI	H	P(O)(OC <sub>2</sub> H <sub>5</sub> )(OC <sub>3</sub> H <sub>7</sub> -i)	C <sub>11</sub> H <sub>17</sub> O <sub>6</sub> PS 308.3	10.40 10.61	— —	10.04 10.28	72	visc. liq.	308

a) w<sub>Cl</sub> (calc.) 11.02 %, w<sub>Cl</sub> (found) 11.30 %.

VI—XII (Table 1) show a small shoulder at  $\lambda = 245$ — $253$  nm. The absorption maximum at the longer wavelength has been assigned to the  $\pi \leftarrow \pi^*$  and  $n \leftarrow \pi$  electron transition in the 4-pyranone skeleton, respectively. For verification of the 4-pyranone molecule protons H-3 and H-6 in the <sup>1</sup>H NMR spectra are important. The individual signals were found in the region  $\delta = 6.37$ — $6.44$  (s, 1H, H-3) and  $8.00$ — $8.06$  (s, 1H, H-6).

The results of tests for pesticide activity confirmed that compounds VI and VII of the group of alkyl esters of dithiocarbamic acid showed an effect on *Alternaria* species comparable to Dithian M-45, which

was used as standard. Compound XXI belonging to the group of esters of organophosphonic acid showed in testing for contact insecticide activity on *Macrosiphoniella sanbornii* the activity of the same order as the standard (Metation E-50). Tests for acaricidal activity of derivatives XV and XIX confirmed their lower activity in comparison with the standard (Akarition E-20). No measurable herbicidal activity was observed at all tested compounds.

## EXPERIMENTAL

Kojic acid was commercial chemical (LIKO,

Bratislava), 2-chloromethyl derivative of kojic acid was prepared according to the Kipnis reaction [5], 5-methoxy-2-chloromethyl-4*H*-pyran-4-one according to [6]. The following starting salts of the respective acids were synthesized by the published procedures: potassium salts of *O*-dialkyldithiocarbonic acid [7], sodium salts of dithiocarbamic acid [8], sodium salts of *O,O*-dialkyl(diphenyl)dithiophosphoric acid [9], and sodium salts of *O,O*-dialkylthiophosphoric acid [10]. Melting points (not corrected) were measured on a Kofler hot stage. Samples for elemental analysis were dried over phosphorous pentoxide (30–50 °C; 2 kPa) for 8–10 h. Reaction course and purity of compounds were monitored by thin-layer chromatography (Silufol UV<sub>254</sub> sheets, Kavalier, Votice) using the solvent system toluene–acetone ( $\varphi_r = 7 : 3$ ). IR spectra (KBr pellets) were taken on the spectrophotometer Specord 80 (Zeiss, Jena), ultraviolet spectra of metanolic solutions were recorded on spectrophotometer M 20 (Zeiss, Jena). <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>) were measured on the spectrometer model BS 487 (Tesla) with HMSDO as an internal standard, MS spectra were recorded on spectrometer MS 902 (AS Kratos) using all-glass heated inlet system with the temperature of an ion source 90–120 °C. Electron energy was 70 eV, trap current 100  $\mu$ A.

Pesticide activity was tested according to the published procedure [11–13].

#### Disodium Salt of *O*-Ethyl-*O*-isopropylthiophosphoric Acid

To the solution of NaOH (16 g; 0.4 mol) in water (100 cm<sup>3</sup>) dioxane (100 cm<sup>3</sup>) was added and under the stirring *O*-ethyl-*O*-isopropylchlorothiophosphate (40.5 g; 0.2 mol), too. Reaction mixture was stirred for 5 h at 60 °C. Dioxane and water were removed from the reaction mixture by distillation under the reduced pressure. Toluene (200 cm<sup>3</sup>) was added to the rest and traces of water were removed by azeotropic distillation. The separated NaCl was filtered off, to the filtrate cyclohexane (60 cm<sup>3</sup>) was added, white crystalline substance was filtered off, washed with cyclohexane and dried *in vacuo*. Yield = 31.9 g (75.2 %).

#### Sodium Salt of Ethyl-*S*-ethylthiophosphoric Acid

NaOH (8 g; 0.2 mol) dissolved in water (80 cm<sup>3</sup>) was added to the stirred solution of *O*-ethylchlorodithiophosphate (20.5 g; 0.01 mol) in dioxane (60 cm<sup>3</sup>). Reaction mixture was stirred for 5 h at the temperature 60 °C. Next procedure is the same as in the preparation of sodium salt of *O*-ethyl-*O*-isopropylthiophosphoric acid. Yield = 18.6 g (89.4 %).

#### Potassium Salt of Ethyl-*O*-ethylthiophosphonic Acid

To the stirred mixture of *O*-ethylthiophosphonic acid (17 g; 0.1 mol) in dry benzene (100 cm<sup>3</sup>) potassium ethoxylate (3.9 gramatom K, 80 cm<sup>3</sup> ethanol) was added at the temperature 15 °C. Ethanol was removed by azeotropic distillation with benzene, the reaction mixture was cooled, and the filtered salt was dried under reduced pressure. Yield = 15.8 g (75.8 %).

#### Synthesis of the Compounds I–XXI

To the stirred solution of the alkaline salt of corresponding acid (0.04 mol) in 80 cm<sup>3</sup> of solvent (acetone, ethyl methyl ketone, acetonitrile) 5-hydroxy-2-chloromethyl-4*H*-pyran-4-one or its substituted derivative was added at once. The reaction mixture was stirred for 8 h under reflux in the used solvent. The reaction course was monitored by thin-layer chromatography. The solvent was removed from the reaction mixture under reduced pressure and water (100 cm<sup>3</sup>) was added to the rest under intensive stirring. If the product was solid and not soluble in water, it was filtered off and recrystallized. In the case that the product was insoluble in water, but liquid, chloroform (80 cm<sup>3</sup>) was added to the aqueous layer and the mixture was thoroughly extracted. Chloroform layer was separated, washed with water and dried. Chloroform and rests of solvents were distilled off *in vacuo* and the product was definitely dried at 80 °C and 13.3 Pa.

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