

Synthesis and biological properties of aryl and pyridazinyl sulfonates

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Substituted aryl and 3-oxo-2*H*-pyridazin-5-yl alkane-, arene-, and phenylmethanesulfonates were synthesized and tested for insecticidal, acaricidal, ovicidal, fungicidal, and herbicidal efficacies.

Among the great many chemical preparations serving to chemical protection of agricultural produces, only a small number of aromatic sulfonates could be found. So far, 4-chlorophenyl benzenesulfonate as ovicide [1] and 4-chlorophenyl 4-chlorobenzenesulfonate, which has beside ovicidal also good acaricidal efficacy [2], have been practically used.

It is clear from many works in patent and technical literature that esters of sulfonic acid as pesticides have been thoroughly studied lately. Regarding the relatively good attainability of sulfonyl chlorides as well as substituted phenols and 5-hydroxy-2*H*-pyridazin-3-ones, we decided to prepare several esters of sulfonic acid (Scheme 1) chemically characterized in Tables 1–6, biologically in Tables 7–10 with purpose to test for biological activity.



R = methyl, ethyl, chloromethyl, 2,3-dichloropropyl, 2-chloroethyl, phenyl, 4-tolyl, 4-halogenophenyl, 2,3,4-trichlorophenyl, 2,4,5-trichlorophenyl, 3-nitrophenyl, and benzyl.

R¹ = chloro, methoxy, ethylthio, phenoxy.

R² = methyl, phenyl.

R³ = methyl, *sec*-butyl, cyclohexyl.

X = halo, nitro, cyano.

Scheme 1

General methods of ester preparation, mainly the reaction of the appropriate alkane- and arenesulfonyl chloride, respectively, with the sodium or potassium salt of the corresponding phenol or 5-hydroxy-2*H*-pyridazin-3-one were used to synthesize the compounds present in Tables 1–6. The resulting products were liquids or crystalline compounds that could be easily isolated.

Different procedure was used to prepare 2,6-dihalogeno-4-cyanophenyl esters. Phenol and sulfonyl chloride were treated with aqueous solution of alkaline hydroxide in a heterogeneous phase. The obtained products were white crystalline compounds.

Table 1
 Characterization of 2-R²-4-R¹-3-oxo-2*H*-pyridazin-5-yl R-sulfonates

Compound	R	R ¹	R ²	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
						% N	% S	% Cl		
<i>I</i>	Methyl	Chloro	Methyl	C ₆ H ₇ ClN ₂ O ₄ S	238.63	11.73 12.80	13.40 13.57	14.83 14.61	55.1	102–104 Ethanol
<i>II</i>	Methyl	Chloro	Phenyl	C ₁₁ H ₉ ClN ₂ O ₄ S	300.70	9.33 9.63	10.67 10.40	11.81 12.03	87.1	121–123 Ethanol
<i>III</i>	Ethyl	Chloro	Phenyl	C ₁₂ H ₁₁ ClN ₂ O ₄ S	314.72	8.90 9.26	10.15 10.31	11.28 11.48	87.7	128–130 Benzene
<i>IV</i>	Ethyl	Methoxy	Phenyl	C ₁₃ H ₁₅ N ₂ O ₅ S	311.32	9.04 8.89	10.31 10.37	— —	63.6	51–53 Ethanol
<i>V</i>	Chloromethyl	Chloro	Methyl	C ₆ H ₆ Cl ₂ N ₂ O ₄ S	273.08	10.26 10.02	11.72 11.56	26.00 26.12	55.1	108–110 Ethanol
<i>VI</i>	Chloromethyl	Chloro	Phenyl	C ₁₁ H ₈ Cl ₂ N ₂ O ₄ S	335.22	8.36 8.11	9.55 9.77	21.18 20.86	98.0	116–118 Ethanol
<i>VII</i>	Chloromethyl	Methoxy	Phenyl	C ₁₂ H ₁₁ ClN ₂ O ₅ S	330.72	8.48 8.67	9.70 9.77	10.75 10.91	94.2	85–87 Ethanol
<i>VIII</i>	Phenyl	Chloro	Methyl	C ₁₁ H ₉ ClN ₂ O ₄ S	300.70	9.35 9.35	10.67 10.37	11.81 11.60	90.1	79–81 Ethanol
<i>IX</i>	Phenyl	Chloro	Phenyl	C ₁₆ H ₁₁ ClN ₂ O ₄ S	362.76	7.72 8.09	8.81 9.01	9.77 9.19	77.4	96–98 Ethanol
<i>X</i>	Phenyl	Methoxy	Phenyl	C ₁₇ H ₁₄ N ₂ O ₅ S	358.35	7.81 7.83	8.93 9.09	— —	73.0	84–86 Ethanol
<i>XI</i>	4-Tolyl	Chloro	Methyl	C ₁₂ H ₁₁ ClN ₂ O ₄ S	314.72	8.90 8.96	10.15 10.35	11.28 11.40	55.7	108–110 Ethanol

Table 1 (Continued)

Compound	R	R ¹	R ²	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
						% N	% S	% Cl		
XII	4-Tolyl	Chloro	Phenyl	C ₁₇ H ₁₃ ClN ₂ O ₄ S	376.78	7.44 7.12	8.51 8.00	9.41 9.01	74.2	118–119 Ethanol
XIII	4-Chlorophenyl	Chloro	Phenyl	C ₁₆ H ₁₀ Cl ₂ N ₂ O ₄ S	397.21	7.05 7.25	8.06 7.98	17.85 17.85	97.1	108–110 Ethanol
XIV	3-Nitrophenyl	Chloro	Phenyl	C ₁₆ H ₁₀ ClN ₃ O ₆ S	407.77	11.60 11.67	7.73 7.65	8.57 9.01	75.1	119–121 Toluene
XV	2,4,6-Trichlorophenyl	Chloro	Phenyl	C ₁₆ H ₈ Cl ₄ N ₂ O ₄ S	466.09	6.01 6.18	6.87 6.86	30.40 30.43	94.4	194–197 Toluene
XVI	2,3,4-Trichlorophenyl	Methoxy	Phenyl	C ₁₇ H ₁₁ Cl ₃ N ₂ O ₅ S	461.67	6.07 6.21	6.94 7.21	23.02 23.19	70.0	115–118 Ethanol
XVII	Benzyl	Chloro	Methyl	C ₁₂ H ₁₁ ClN ₂ O ₄ S	314.72	8.90 9.27	10.15 10.24	11.28 11.11	62.0	125–128 Methanol
XVIII	Benzyl	Methoxy	Phenyl	C ₁₆ H ₁₆ N ₂ O ₅ S	372.37	7.54 7.36	8.62 8.41	— —	80.0	117–119 Ethanol
XIX	Benzyl	Chloro	Phenyl	C ₁₇ H ₁₃ ClN ₂ O ₄ S	376.78	7.44 7.62	8.51 8.37	9.41 9.32	43.3	153–154 Ethanol
XX	Benzyl	Phenoxy	Phenyl	C ₂₃ H ₁₈ N ₂ O ₅ S	434.45	6.46 6.68	7.38 7.01	— —	80.4	168–170 Acetonitrile
XXI	Benzyl	Ethylthio	Phenyl	C ₁₉ H ₁₈ N ₂ O ₄ S ₂	402.47	6.95 7.15	16.00 16.35	— —	59.6	88–90 Methanol
XXII	Benzyl	Ethylthio	Methyl	C ₁₄ H ₁₆ N ₂ O ₄ S ₂	340.40	8.23 8.12	18.82 19.04	— —	73.3	79–81 Ethanol–water

Table 2
2,6-Di-X-4-cyanophenyl R-sulfonate.

Compound	R	X	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
					% N	% S	% X		
XXIII	Methyl	Bromo	C ₈ H ₅ Br ₂ NO ₃ S	355.00	3.95 4.16	9.02 9.12	45.01 44.84	84.7	163–165 Ethanol
XXIV	Methyl	Iodo	C ₈ H ₅ I ₂ NO ₃ S	447.00	3.12 3.51	7.13 7.30	56.45 56.02	87.6	191–194 Ethanol–acetone
XXV	Ethyl	Bromo	C ₁₀ H ₇ Br ₂ NO ₃ S	369.02	3.79 4.17	8.68 8.57	43.22 43.44	86.6	121–123 Acetone–ethanol
XXVI	Ethyl	Iodo	C ₁₀ H ₇ I ₂ NO ₃ S	461.02	3.03 3.21	6.91 7.17	54.76 55.19	72.7	142–144 Acetone–ethanol
XXVII	Chloromethyl ^a	Bromo	C ₈ H ₄ Br ₂ ClNO ₃ S	389.45	3.60 3.49	8.22 8.57	41.10 41.25	71.2	179–181 Ethanol–dioxan
XXVIII	Chloromethyl ^b	Iodo	C ₈ H ₄ ClI ₂ NO ₃ S	481.45	2.89 2.69	6.63 6.48	52.45 52.37	85.0	137–139 Ethanol
XXIX	Phenyl	Bromo	C ₁₃ H ₇ Br ₂ NO ₃ S	417.07	3.35 3.57	7.68 7.79	38.40 38.07	80.2	140–142 Ethanol
XXX	Phenyl	Iodo	C ₁₃ H ₇ I ₂ NO ₃ S	511.07	2.74 3.08	6.26 6.55	49.61 50.27	91.9	171–173 Ethanol–acetone
XXXI	4-Tolyl	Bromo	C ₁₄ H ₉ Br ₂ NO ₃ S	431.09	3.25 3.38	7.42 7.22	37.10 37.58	86.4	144–146 Ethanol
XXXII	4-Tolyl	Iodo	C ₁₄ H ₉ I ₂ NO ₃ S	525.09	2.68 2.71	6.09 6.37	48.24 48.71	77.1	154–155 Ethanol–dioxan
XXXIII	4-Chlorophenyl ^c	Iodo	C ₁₃ H ₆ ClI ₂ NO ₃ S	545.52	2.57 2.72	5.86 6.07	46.45 46.85	87.7	169–171 Ethanol–dioxan
XXXIV	4-Bromophenyl	Bromo	C ₁₃ H ₆ Br ₃ NO ₃ S	495.98	2.82 2.51	6.45 6.19	48.25 48.35	87.8	160–161 Ethanol–acetone

Table 2 (Continued)

Compound	R	X	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
					% N	% S	% X		
XXXV	3-Nitrophenyl	Bromo	C ₁₃ H ₆ Br ₂ N ₂ O ₅ S	462.06	6.06 6.35	6.93 7.14	34.61 34.58	71.6	174–176 Ethanol–acetone
XXXVI	3-Nitrophenyl	Iodo	C ₁₃ H ₆ I ₂ N ₂ O ₅ S	556.06	5.04 4.81	5.75 6.08	45.60 46.06	87.6	191–192 Methanol–acetone
XXXVII	2,3,4-Trichloro- phenyl ^d	Iodo	C ₁₃ H ₃ Cl ₃ I ₂ NO ₅ S	614.39	2.28 2.47	5.22 5.48	41.13 42.02	86.5	175–177 Ethanol–dioxan
XXXVIII	Benzyl	Bromo	C ₁₄ H ₉ Br ₂ NO ₅ S	431.09	3.25 3.36	7.42 7.63	37.10 37.44	68.0	>200 decomposition
XXXIX	Benzyl	Iodo	C ₁₄ H ₉ I ₂ NO ₅ S	525.09	2.68 2.97	6.09 6.38	48.24 48.19	29.0	165–170 Ethanol–acetone

a) Calculated: 9.11% Cl;
found: 9.37% Cl.

b) Calculated: 7.33% Cl;
found: 7.31% Cl.

c) Calculated: 6.49% Cl;
found: 6.54% Cl.

d) Calculated: 17.33% Cl;
found: 17.68% Cl.

Table 3
2,6-Di-X-3-R^a-4-nitrophenyl R-sulfonates

Compound	R	X	R ^a	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
						% N	% S	% X		
<i>XL</i>	Methyl	Chloro	Hydrogen	C ₇ H ₅ Cl ₂ NO ₅ S	286.07	4.88	11.19	24.75	88.0	88-90
<i>XLI</i>	Methyl	Bromo	Hydrogen	C ₇ H ₅ Br ₂ NO ₅ S	374.99	3.73	8.53	42.60	90.0	Ethanol 138-140
<i>XLII</i>	Methyl	Bromo	Methyl	C ₈ H ₇ Br ₂ NO ₅ S	389.01	3.93	8.61	42.63	82.7	Ethanol 82-84
<i>XLIII</i>	Ethyl	Bromo	Hydrogen	C ₈ H ₇ Br ₂ NO ₅ S	389.01	3.61	8.22	41.01	88.0	Ethanol 108-110
<i>XLIV</i>	Ethyl	Bromo	Methyl	C ₉ H ₉ Br ₂ NO ₅ S	403.03	4.14	8.40	41.31	83.3	Ethanol-acetone 81-83
<i>XLV</i>	Chloromethyl ^a	Bromo	Hydrogen	C ₇ H ₄ Br ₂ ClNO ₅ S	409.43	3.63	8.20	40.06	76.6	Ethanol 157-159
<i>XLVI</i>	Chloromethyl ^b	Bromo	Methyl	C ₈ H ₆ Br ₂ ClNO ₅ S	423.45	3.44	7.85	39.21	76.7	Ethanol 103-105
<i>XLVII</i>	Phenyl	Chloro	Hydrogen	C ₁₂ H ₇ Cl ₂ NO ₅ S	348.14	3.61	7.56	37.70	98.0	Cyclohexane ^c 121-123
<i>XLVIII</i>	Phenyl	Bromo	Hydrogen	C ₁₂ H ₇ Br ₂ NO ₅ S	437.06	4.30	9.32	19.98	71.3	Ethanol 127-129
<i>XLIX</i>	Phenyl	Bromo	Methyl	C ₁₃ H ₉ Br ₂ NO ₅ S	451.08	3.31	7.45	36.50	85.2	Ethanol-acetone 136-138
<i>L</i>	4-Tolyl	Bromo	Hydrogen	C ₁₃ H ₉ Br ₂ NO ₅ S	451.08	3.03	7.23	36.00	92.4	Ethanol-acetone 131-133
<i>LI</i>	4-Tolyl	Bromo	Methyl	C ₁₄ H ₁₁ Br ₂ NO ₅ S	465.10	3.11	7.10	35.50	92.1	Acetone 167-169
<i>LII</i>	4-Chlorophenyl ^c	Bromo	Methyl	C ₁₃ H ₈ Br ₂ ClNO ₅ S	485.51	2.91	7.00	33.99	87.3	Ethanol-acetone 164-166
<i>LIII</i>	2,3,4-Trichloro-phenyl ^d	Bromo	Hydrogen	C ₁₂ H ₄ Br ₂ Cl ₃ NO ₅ S	540.38	2.88	6.59	32.95	83.2	Acetone 148-151
<i>LIV</i>	Benzyl	Chloro	Hydrogen	C ₁₃ H ₉ Cl ₂ NO ₅ S	362.16	3.02	6.12	29.54	89.5	Ethanol-acetone 132-134
<i>LV</i>	Benzyl	Bromo	Hydrogen	C ₁₃ H ₉ Br ₂ NO ₅ S	451.08	3.86	8.85	19.58	87.0	Ethanol 109-111
						3.98	9.02	19.48		Acetone
						3.44	6.81	35.38		

a) Calculated: 8.70% Cl;
found: 8.79% Cl.

b) Calculated: 8.38% Cl;
found: 8.58% Cl.

c) Calculated: 7.29% Cl;
found: 7.40% Cl.

d) Calculated: 19.70% Cl;
found: 19.66% Cl.

Table 4
2-X¹-4-X²-6-X³-3-methylphenyl R-sulfonates

Compound	R	X ¹	X ²	X ³	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
							% N	% S	% Cl		
LVI	Methyl	Nitro	Nitro	Hydrogen	C ₈ H ₈ N ₂ O ₇ S	276.22	10.13 10.41	11.56 11.81	— —	92.0	145—146 Ethanol
LVII	Methyl	Hydrogen	Nitro	Nitr	C ₈ H ₈ N ₂ O ₇ S	276.22	10.13 10.31	11.56 11.62	— —	83.8	82—84 Ethanol
LVIII	Methyl	Nitro	Chloro	Nitro	C ₈ H ₇ ClN ₂ O ₇ S	310.66	9.02 9.41	10.30 10.31	11.41 11.45	42.0	129—131 Ethanol
LIX	Ethyl	Nitro	Nitro	Hydrogen	C ₉ H ₁₀ N ₂ O ₇ S	290.24	9.64 9.95	11.02 11.37	— —	70.3	Viscous liquid
LX	Ethyl	Hydrogen	Nitro	Nitro	C ₉ H ₁₀ N ₂ O ₇ S	290.24	9.65 10.03	11.02 11.18	— —	97.0	57—59 Ethanol
LXI	Ethyl	Nitro	Chloro	Nitro	C ₉ H ₉ ClN ₂ O ₇ S	324.68	8.62 8.60	9.84 9.70	10.91 11.14	98.3	110—112 Ethanol
LXII	Ethyl	Hydrogen	Chloro	Nitro	C ₉ H ₁₀ ClNO ₅ S	279.68	5.01 4.93	11.46 11.30	12.65 12.75	87.8	Viscous liquid
LXIII	Chloromethyl	Nitro	Nitro	Hydrogen	C ₈ H ₇ ClN ₂ O ₇ S	310.67	9.03 9.29	10.30 10.51	11.41 11.29	69.0	94—95 Ethanol
LXIV	Chloromethyl	Hydrogen	Nitro	Nitro	C ₈ H ₇ ClN ₂ O ₇ S	310.67	9.03 9.29	10.30 10.11	11.42 11.82	74.7	60—62 Ethanol
LXV	2-Chloroethyl	Nitro	Chloro	Nitro	C ₉ H ₈ Cl ₂ N ₂ O ₇ S	359.12	7.80 7.40	8.92 9.38	19.72 19.42	21.7	53—55 Ethanol
LXVI	Phenyl	Hydrogen	Chloro	Nitro	C ₁₃ H ₁₀ ClNO ₅ S	327.72	4.27 4.53	9.78 9.97	10.82 11.04	98.2	111—113 Ethanol
LXVII	Phenyl	Nitro	Nitro	Hydrogen	C ₁₃ H ₁₀ N ₂ O ₇ S	338.28	8.28 8.57	9.46 9.67	— —	91.8	102—104 Ethanol

Table 4 (Continued)

Compound	R	X ¹	X ²	X ³	Formula	M	Calculated/Found			Yield [%]	M.p. [°C]
							% N	% S	% Cl		
LXVIII	Phenyl	Hydrogen	Nitro	Nitro	C ₁₃ H ₁₀ N ₂ O ₇ S	338.28	8.28 8.54	9.46 9.13	—	89.0	106–108 Ethanol
LXIX	Phenyl	Nitro	Chloro	Nitro	C ₁₃ H ₉ ClN ₂ O ₇ S	372.73	7.50 7.88	8.58 8.31	9.51 9.85	96.7	117–119 Ethanol
LXX	4-Tolyl	Hydrogen	Chloro	Nitro	C ₁₄ H ₁₂ ClNO ₅ S	341.74	4.11 4.31	9.37 9.68	10.38 10.68	96.5	102–104 Ethanol
LXXI	4-Tolyl	Nitro	Nitro	Hydrogen	C ₁₄ H ₁₂ N ₂ O ₇ S	352.30	7.94 8.11	9.07 9.19	—	93.6	106–108 Ethanol
LXXII	4-Tolyl	Hydrogen	Nitro	Nitro	C ₁₄ H ₁₂ N ₂ O ₇ S	352.30	7.94 7.76	9.07 9.38	—	89.0	127–128 Ethanol
LXXIII	4-Tolyl	Nitro	Chloro	Nitro	C ₁₄ H ₁₁ ClN ₂ O ₇ S	386.74	7.23 7.60	8.28 8.32	9.17 9.26	87.3	125–127 Ethanol
LXXIV	4-Chlorophenyl	Hydrogen	Chloro	Nitro	C ₁₃ H ₉ Cl ₂ NO ₅ S	362.16	3.86 4.03	8.83 9.19	19.56 19.35	96.3	79–80 Ethanol
LXXV	4-Chlorophenyl	Hydrogen	Nitro	Nitro	C ₁₃ H ₉ ClN ₂ O ₇ S	372.72	7.52 7.30	8.60 8.73	9.52 9.43	76.8	120–122 Ethanol
LXXVI	4-Bromophenyl ^a	Nitro	Nitro	Hydrogen	C ₁₃ H ₉ BrN ₂ O ₇ S	417.18	6.71 7.09	7.68 7.85	—	80.0	108–110 Ethanol
LXXVII	4-Bromophenyl ^b	Nitro	Chloro	Nitro	C ₁₃ H ₈ BrClN ₂ O ₇ S	451.62	6.21 6.59	7.08 7.04	7.85 8.24	89.6	152–154 Acetone
LXXVIII	Benzyl	Nitro	Chloro	Nitro	C ₁₄ H ₁₁ ClN ₂ O ₇ S	386.73	7.23 7.09	8.28 8.04	9.17 9.21	22.0	106–108 Ethanol

a) Calculated: 19.16% Br;
found: 19.22% Br.

b) Calculated: 17.70% Br;
found: 18.10% Br.

Table 5
2-R³-4,6-Dinitrophenyl R-sulfonates

Compound	R	R ³	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
					% N	% S	% Cl		
LXXXIX	Methyl	Methyl	C ₈ H ₈ N ₂ O ₇ S	276.21	10.13 10.55	11.58 11.87	— —	50.7	146–148 Ethanol
LXXX	Methyl	<i>n</i> -Butyl	C ₁₁ H ₁₄ N ₂ O ₇ S	318.27	8.78 8.62	10.03 9.81	— —	91.6	Viscous liquid
LXXXI	Methyl	Cyclohexyl	C ₁₃ H ₁₆ N ₂ O ₇ S	344.33	8.13 8.52	9.29 9.62	— —	98.0	130–132 Ethanol
LXXXII	Methyl	1-Methylheptyl	C ₁₅ H ₂₂ N ₂ O ₇ S	374.42	7.48 7.38	8.54 8.54	— —	56.8	Viscous liquid
LXXXIII	Ethyl	Methyl	C ₉ H ₁₀ N ₂ O ₇ S	290.23	9.64 9.32	11.02 11.30	— —	73.2	70–72 Ethanol
LXXXIV	Ethyl	<i>sec</i> -Butyl	C ₁₂ H ₁₆ N ₂ O ₇ S	332.29	8.42 8.60	9.62 9.91	— —	64.6	62–64 Ethanol
LXXXV	Ethyl	Cyclohexyl	C ₁₄ H ₁₈ N ₂ O ₇ S	358.35	7.81 7.71	8.93 9.01	— —	86.7	126–127 Ethanol
LXXXVI	Chloromethyl	Methyl	C ₈ H ₇ ClN ₂ O ₇ S	310.66	9.03 9.37	10.31 10.12	11.45 11.62	61.5	79–81 Ethanol
LXXXVII	Chloromethyl	<i>sec</i> -Butyl	C ₁₁ H ₁₃ ClN ₂ O ₇ S	352.73	7.94 7.70	9.06 9.31	10.05 10.01	82.3	Viscous liquid
LXXXVIII	Chloromethyl	Cyclohexyl	C ₁₃ H ₁₅ ClN ₂ O ₇ S	378.78	7.40 7.80	8.45 8.71	9.56 10.05	56.2	90–91.5 Ethanol
LXXXIX	2-Chloroethyl	<i>sec</i> -Butyl	C ₁₂ H ₁₅ ClN ₂ O ₇ S	366.74	7.63 8.07	9.67 9.50	8.07 8.41	66.1	Viscous liquid
XC	2-Chloroethyl	1-Methylheptyl	C ₁₆ H ₂₃ ClN ₂ O ₇ S	422.87	6.62 7.01	7.58 7.25	8.41 8.70	62.6	Viscous liquid

Table 5 (Continued)

Compound	R	R ³	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
					% N	% S	% Cl		
<i>XCI</i>	2,3-Dichloropropyl	<i>sec</i> -Butyl	C ₁₃ H ₁₆ Cl ₂ N ₂ O ₇ S	399.10	7.01 6.96	8.01 8.40	17.72 17.57	87.5	Viscous liquid
<i>XCII</i>	Phenyl	<i>sec</i> -Butyl	C ₁₆ H ₁₆ N ₂ O ₇ S	380.36	7.37 7.80	8.41 8.60	— —	97.4	82—84 Ethanol
<i>XCIII</i>	Phenyl	1-Methylheptyl	C ₂₀ H ₂₄ N ₂ O ₇ S	436.45	6.42 6.38	7.32 6.98	— —	63.8	Viscous liquid
<i>XCIV</i>	4-Tolyl	<i>sec</i> -Butyl	C ₁₇ H ₁₈ N ₂ O ₇ S	394.38	7.11 7.44	8.12 8.23	— —	91.8	116—118 Ethanol
<i>XCV</i>	4-Chlorophenyl	<i>sec</i> -Butyl	C ₁₆ H ₁₅ ClN ₂ O ₇ S	414.81	6.76 6.43	7.73 8.01	8.58 8.90	95.0	97—99 Ethanol
<i>XCVI</i>	2,4,5-Trichloro-phenyl	1-Methylheptyl	C ₂₀ H ₂₁ Cl ₃ N ₂ O ₇ S	539.78	5.19 4.91	5.93 6.00	19.72 20.02	67.3	Viscous liquid
<i>XCVII</i>	Benzyl	<i>sec</i> -butyl	C ₁₇ H ₁₈ N ₂ O ₇ S	394.38	7.11 6.83	8.12 8.56	— —	72.8	Viscous liquid

Table 6
X-Phenyl R-sulfonates

Compound	R	X	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
					% N	% S	% Cl		
XCVIII	Methyl	2,4,5-Trichloro-6-nitro	C ₇ H ₃ Cl ₃ NO ₅ S	320.51	4.37	10.00	33.15	96.7	133—135
					4.62	10.16	32.75		Ethanol
XCIX	Ethyl	3-Trifluoromethyl-4-chloro	C ₉ H ₈ ClF ₃ O ₃ S	288.66	—	11.08	12.28	80.4	Liquid
					—	10.88	12.70		
C	Ethyl	2,4,5-Trichloro-6-nitro	C ₈ H ₆ Cl ₃ NO ₅ S	334.53	4.18	9.56	31.79	95.2	106—108
					4.45	9.71	32.01		Ethanol
CI	Ethyl	2,6-Dinitro-4- <i>tert</i> -butyl	C ₁₂ H ₁₆ N ₂ O ₇ S	332.29	8.42	9.62	—	92.8	120—122
					8.71	10.08	—		Ethanol
CII	Ethyl	2-Chloro-4- <i>tert</i> -butyl-6-nitro	C ₁₂ H ₁₆ ClNO ₅ S	321.76	4.36	9.96	11.02	69.2	Liquid
					4.81	10.14	11.20		
CIII	Chloromethyl	3-Trifluoromethyl-4,6-dichloro	C ₈ H ₄ Cl ₃ F ₃ O ₃ S	343.52	—	9.27	30.80	97.7	Liquid
					—	8.97	30.98		
CIV	Chloromethyl	2,4,5-Trichloro-6-nitro	C ₇ H ₃ Cl ₄ NO ₅ S	354.96	3.95	9.01	39.90	94.7	102—104
					3.99	9.20	40.14		Ethanol
CV	Chloromethyl	3-Trifluoromethyl-4-chloro	C ₈ H ₅ Cl ₂ F ₃ O ₃ S	309.07	—	10.46	22.95	80.8	Liquid
					—	10.46	22.64		
CVI	Phenyl	2,4,5-Trichloro-6-nitro	C ₁₂ H ₆ Cl ₃ NO ₅ S	382.58	3.66	8.37	27.80	81.7	169—170*
					3.42	8.63	27.63		Ethanol—acetone
CVII	Phenyl	2-Methylthiomethyl	C ₁₄ H ₁₄ O ₃ S ₂	294.37	—	21.78	—	85.4	Liquid
					—	21.49	—		

Table 6 (Continued)

Compound	R	X	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
					% N	% S	% Cl		
<i>CVIII</i>	Phenyl	3-Trifluoromethyl-4-chloro	$C_{13}H_8ClF_3O_3S$	336.70	—	9.47	10.52	83.7	51—53
					—	9.36	11.07		Hexane
<i>CLIX</i>	Phenyl	3-Trifluoromethyl-4,6-dichloro	$C_{13}H_7Cl_2F_3O_3S$	371.15	—	8.62	19.12	83.2	Liquid
					—	9.01	19.30		
<i>CX</i>	4-Tolyl	3-Trifluoromethyl-4-chloro	$C_{14}H_{10}ClF_3O_3S$	350.72	—	9.12	9.97	68.6	78—80
					—	9.07	10.12		Ethanol
<i>CXI</i>	4-Tolyl	2-Methylthiomethyl	$C_{15}H_{16}O_3S_2$	308.39	—	20.78	—	99.0	Liquid
					—	20.36	—		
<i>CXII</i>	4-Tolyl	2,4,5-Trichloro-6-nitro	$C_{13}H_6Cl_3NO_5S$	396.60	3.53	8.07	26.80	76.8	150—151
					3.62	8.40	27.01		Ethanol—acetone**
<i>CXIII</i>	4-Chlorophenyl	2,4,5-Trichloro-6-nitro	$C_{12}H_5Cl_4NO_5S$	417.03	3.36	7.68	34.00	89.0	118—120
					3.33	7.59	33.68		Ethanol—acetone
<i>CXIV</i>	Benzyl	2,4,5-Trichloro-6-nitro	$C_{13}H_8Cl_3NO_5S$	396.60	3.53	8.07	26.80	88.0	134—136
					3.91	8.14	26.36		Methanol
<i>CXV</i>	Benzyl ^a	2,4,5-Trichloro-6-bromo	$C_{13}H_8BrCl_3O_3S$	430.51	—	7.44	24.70	93.0	115—116
					—	7.49	25.01		Ethanol
<i>CXVI</i>	Benzyl ^b	2,4,5-Trichloro-6-iodo	$C_{13}H_8Cl_3IO_3S$	477.51	—	6.70	22.24	91.0	146—149
					—	6.88	22.59		Acetonitrile
<i>CXVII</i>	Benzyl	Pentachloro	$C_{13}H_7Cl_5O_3S$	420.50	—	7.62	42.20	85.0	154—156
					—	8.11	42.28		Acetonitrile

* Ref. [5] gives m.p. 171—171.5°C.

** Ref. [5] gives m.p. 152.3—152.6°C.

a) Calculated: 18.55% Br;
found: 18.37% Br.b) Calculated: 26.53% I;
found: 26.95% I.

We found that pyridazinyl sulfonates (Table 1) showed orderly lower biological efficiency than the used standard.

2,6-Dihalogeno-4-cyanophenyl esters (Table 2) showed good herbicidal properties which were in some cases equal to those of the used standards. The most active from this group was 2,6-diiodo-4-cyanophenyl chloromethanesulfonate (XXVIII) (Table 10).

The herbicidal efficacy of 2,6-dihalogeno-3-alkyl-4-nitrophenyl esters (Table 3) was measurable but lower than that of the used standards. Remarkable was the acaricidal efficiency of 2,6-dibromo-4-nitrophenyl phenylmethanesulfonate (LV) which was only a little less active than the used standard (Table 7).

Some of the 2,4,6-substituted 3-methylphenyl esters (Table 4) showed measurable herbicidal efficacy but lower than the used standard. The acaricidal (Table 7) and mainly fungicidal efficacy of 2,6-dinitro-3-methyl-4-chlorophenyl 2-chloroethanesulfonate (LXV) to *Sclerotinia fructicola* (Wint.) Rehm (ED₅₀ 0.039, standard Kaptan 0.036) is worth mentioning.

Biologically the most interesting group was that of 2-alkyl-4,6-dinitrophenyl esters (Table 5) from which 2-alkyl-4,6-dinitrophenyl alkanesulfonates showed very good herbicidal efficacies being only a little lower than that of the used standard. On the other hand, halogenoalkanesulfonates were very effective as acaricides, even more efficient than the used standard. It concerned 2-*sec*-butyl-4,6-dinitrophenyl 2-chloroethanesulfonate (LXXXIX), the appropriate chloromethanesulfonate (LXXXVII), and 2,3-dichloropropanesulfonate (XCI) (Table 7). Similarly, their fungicidal efficacies were also very good. Compounds LXXXVII and XCI as seed-dressing were more effective than the used standard (Table 8).

Further tests with these compounds as seed-dressing are in progress. From this group of compounds, 2-(1-methylheptyl)-4,6-dinitrophenyl 2,4,5-trichlorobenzenesulfonate (XCVI) and the appropriate 2-chloroethanesulfonate (XC) (Table 9) were very efficient also as antipowdery mildew fungicides.

Table 7

Acaricidal efficacy of some compounds on *Tetranychus urticae* Koch

Compound	LXV	XCVI	XC	LV	LXXXIX	XCI	LXXXVII	Acrex — Standard
LC ₅₀ p.p.m.	0.01	0.01	0.01	0.00791	0.000759	0.0039	0.00219	0.005

Table 8

Fungicidal efficacy of some compounds (as seed-dressing) on *Fusarium nivale* (Fr.) Ces.

Compound	XC	LXXXIX	XCI	LXXXVII	Methylenedirhodanide — Standard
ED ₅₀ p.p.m.	13.4	12.5	4.0		6.9

Table 9
Antipowdery mildew efficacy of chosen compounds

Compound	<i>Erysiphe graminis</i>	<i>Erysiphe cichoracearum</i>
	ED ₅₀ p.p.m.	ED ₅₀ p.p.m.
XC	21.4	5.6
XCVI	105.0	<0.5
Acrex — Standard	17.5	<0.5

Table 10
Herbicidal efficacy of 2,6-diiodo-4-cyanophenyl chloromethanesulfonate (XXVIII)

Testing object	Postemergence application				Preemergence application	
	XXVIII		Standard		5 kg/ha	
	5 kg/ha	0.1 kg/ha	5 kg/ha	0.1 kg/ha	XXVIII	Standard
<i>Avena sativa</i> L.	4	0	4	0	0	1.5
<i>Echinochloa crus-galli</i> L. P. Beauv.	-	0	-	1	0	0
<i>Beta vulgaris</i> L.	-	-	5	5	5	5
<i>Polygonum persicaria</i> L.	-	-	5	5	5	5
<i>Chenopodium album</i> L.	-	5	-	-	5	5
<i>Brassica denacea</i> L.	5	2	-	5	5	5
<i>Pisum sativum</i> L.	4	0	-	1	0	0
<i>Avena fatua</i> L.	5	0	5	0	0	0
<i>Hordeum sativum</i> L.	3	0	1	0	0	0
<i>Vicia sativa</i> L.	-	4	5	2.5	0	0
<i>Fagopyrum sagittatum</i> L.	-	-	-	-	0	5
<i>Sinapis alba</i> L.	-	-	-	-	5	5
<i>Amaranthus retroflexus</i> L.	-	5	-	5	5	5
<i>Linum usitatissimum</i> L.	-	0	-	0	0	0
<i>Zea mays</i> L.	-	0	5	0	0	0
<i>Triticum sativum</i> L.	-	0	1	0	0	0

Standard — Joxynil.

Classification scale 0—5 (0 — intact; 5 — totally perished).

We failed to prove fungicidal and herbicidal efficacies of aryl sulfonates (Table 6) in conditions of our experiments. Measurable herbicidal activity was found only with 2,4,5-trichloro-6-nitrophenyl alkanesulfonates.

Experimental

The analytical and physical characteristics of the synthesized compounds are in Tables 1—6. Melting points were determined according to Kofler.

Pesticidal efficacies were determined according to [3, 4] and the following objects were used to test the synthesized compounds: Insecticidal efficacy was followed on *Musca domestica* L., *Calandra granaria* L., systemic insecticidal efficacy on *Macrosypho-*

niella sanborni Gillette, acaricidal efficacy on *Tetranychus urticae* Koch, ovicidal efficacy on the eggs of *Tetranychus urticae* Koch, and contact insecticidal efficacy on *Aphis fabae* Scop.

For determination and comparison of the fungicidal efficacies of the mentioned compounds, *in vitro* as well as *in vivo* methods were used. The inherent efficacy was followed on the spores of *Sclerotinia fructicola* (Wint.) Rehm (slide germination test) and on the spores of *Aspergillus niger* Tiegh, *Fusarium nivale* (Fr.) Ces., *Alternaria* sp., and *Stemphylium sarcinoforme* (Cav.) Withshire fungi. The antipowdery mildew efficacy was tested on the living plants of spring barley, sort Dunajský trh (*Erysiphe graminis* DC.) and on cucumbers, sort Znojenské (*Erysiphe cichoracearum* DC.).

The herbicidal efficacy was determined by the method of preemergence (into the soil) and postemergence (to the leaf) application. The testing objects were: *Avena sativa* L., *Echinochloa crus-galli* L. P. Beauv., *Beta vulgaris* L., *Polygonum persicaria* L., *Chenopodium album* L., *Brassica denacea* L., *Pisum sativum* L., *Avena fatua* L., *Hordeum sativum* L., *Vicia sativa* L., *Fagopyrum sagittatum* L., *Sinapis alba* L., *Amaranthus retroflexus* L., *Linum usitatissimum* L., *Zea mays* L., and *Triticum sativum* L.

Esters of alkane-, arene-, and phenylmethanesulfonic acid (I—XXII, XL—CXVII)

The corresponding sulfonyl chloride (0.1 mole) was added to sodium or potassium salt of the appropriate phenol or 5-hydroxy-2H-pyridazin-3-one (0.1 mole) in acetone (ethyl methyl ketone, acetonitrile, or tetrahydrofuran) (100 ml) under stirring at 15—20°C. This solution was stirred for 1 hour at 20—25°C and then for 1—6 hours under reflux. The formed sodium or potassium chloride was filtered off and the filtrate evaporated under reduced pressure. Benzene or toluene (100—150 ml) was added to the residue, washed with water, 5% solution of sodium carbonate, and water. After drying with sodium sulfate, the solvent was distilled off under reduced pressure. The residue was dried *in vacuo* at 0.3 torr and bath temperature 90°C for 2 hours. The obtained solid was purified by crystallization.

2,6-Dihalogeno-4-cyanophenyl alkane- and arenesulfonates (XXIII—XXXIX)

2,6-Dihalogeno-4-cyanophenol (0.07 mole) was added to sodium hydroxide (0.077 mole) in water (80 ml) and then at 60°C the appropriate sulfonyl chloride (0.07 mole) was added. The temperature was allowed to rise to 93°C and the reaction mixture stirred for 30 minutes. After cooling the solution to 16°C, the obtained product was filtered, washed with water, dried, and crystallized.

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