

Synthesis and pesticidal activity of alkylthiomethylphenyl *N*-methyl- or *N,N*-dimethylcarbamates

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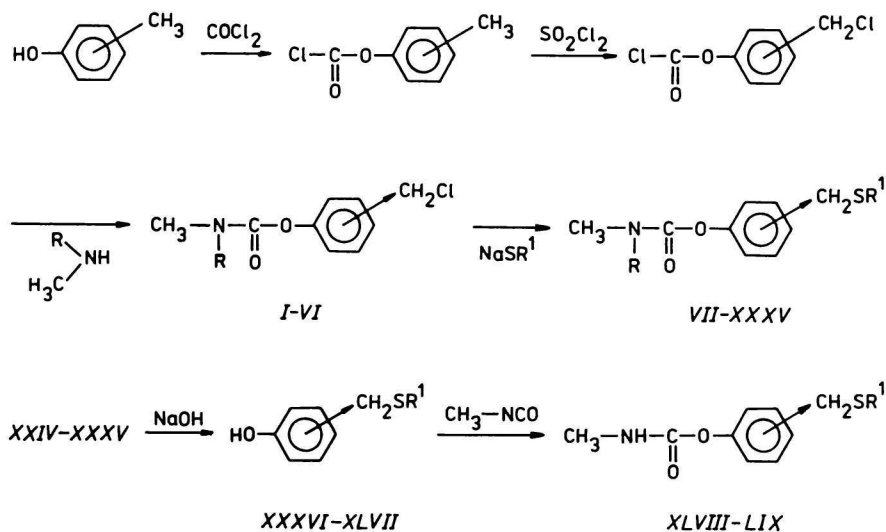
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A synthesis of alkylthiomethylphenyl *N*-methyl- or *N,N*-dimethylcarbamates is described. A pesticidal activity of all compounds prepared was determined. As compared with the standard used the most active on *Aphis fabae* were 2-(methylthiomethyl)phenyl *N,N*-dimethyl-, 2-(ethylthiomethyl)phenyl *N,N*-dimethyl-, 2-(isopropylthiomethyl)phenyl *N,N*-dimethyl-, 2-(methylthiomethyl)phenyl *N*-methyl-, 2-(ethylthiomethyl)phenyl *N*-methyl-, 3-(ethylthiomethyl)phenyl *N*-methyl-, 2-(propylthiomethyl)phenyl *N*-methyl-, and 2-(isopropylthiomethyl)phenyl *N*-methylcarbamates and on *M. sanbornii* (systemic activity) 2-(*tert*-butylthiomethyl)phenyl *N*-methyl- and 2-(ethylthioethylthiomethyl)phenyl *N*-methylcarbamates.

Описан синтез алкилтиометилфенил-*N*-метил- или *N,N*-диметилкарбаматов. Определена пестицидная активность всех полученных соединений. По сравнению с используемым стандартом наиболее активными по отношению к *Aphis fabae* оказались 2-(метилтиометил)фенил-*N,N*-диметил-, 2-(этилтиометил)фенил-*N,N*-диметил-, 2-(изопропилтиометил)фенил-*N,N*-диметил-, 2-(метилтиометил)фенил-*N*-метил-, 2-(этилтиометил)фенил-*N*-метил-, 3-(этилтиометил)фенил-*N*-метил-, 2-(пропилтиометил)фенил-*N*-метил- и 2-(изопропилтиометил)фенил-*N*-метилкарбаматы, а по отношению к *M. sanbornii* (систематическая активность) 2-[*трет*-бутилтиометил]фенил-*N*-метил- и 2-(этилтиоэтилтиометил)фенил-*N*-метилкарбаматы.

From the practical point of view a contact insecticidal agent ethiophencarp with an active compound 2-(ethylthiomethyl)phenyl *N*-methylcarbamate is known [1, 2]. In our work we focused the attention to the synthesis of analogical compounds with the aim to find pesticidal properties. The synthesis of compounds investigated is illustrated in Scheme 1.

Chloromethylphenyl *N*-methyl- or *N,N*-dimethylcarbamates (Table 1) were prepared by the reaction of chloromethylphenyl carbonates with amine and with an aqueous solution of amine, respectively. A preparation using a gaseous amine appeared to be more convenient, by which the yields were by 20 to 30 % higher and the products were more pure.



Scheme 1

Table 1

Characterization of chloromethylphenyl-*N*-methyl- or *N,N*-dimethylcarbamates

| Compound | R | X | $w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$ | | Yield % | M.p./°C B.p./°C(<i>p</i> /Pa) |
|----------|-----------------|---|--|------|------------|-----------------------------------|
| | | | N | Cl | | |
| I | H | 2 | 7.0 | 17.8 | 84.5 | 77—79 |
| | | | 7.1 | 18.0 | | |
| II | H | 3 | 7.0 | 17.8 | 88.4 | 81—82 |
| | | | 7.2 | 18.1 | | |
| III | H | 4 | 7.0 | 17.8 | 81—85 | 100—102 |
| | | | 7.1 | 17.7 | | |
| IV | CH ₃ | 2 | 6.6 | 16.6 | 73.1 | 120—122(20) |
| | | | 6.8 | 16.9 | | |
| V | CH ₃ | 3 | 6.6 | 16.6 | 79.2 | 115(20) |
| | | | 6.5 | 16.5 | | |
| VI | CH ₃ | 4 | 6.6 | 16.6 | 83.4 | 67(69) |
| | | | 6.4 | 16.7 | | |

X is the position of the CH₂Cl group on the benzene ring.

Nucleophilic substitution reactions of chloromethylphenyl *N*-methyl- or *N,N*-dimethylcarbamates with sodium thiophenolate, potassium rhodanide, sodium *O*-ethyl xantogenate, sodium *N,N*-dimethyldithiocarbamide, and sodium salt of *O,O*-dimethyldithiophosphoric acid afforded expected products (Table 2). The substantial difference was obtained by the reaction with sodium alkyl(aryl) mercaptide by which chloromethylphenyl *N,N*-dimethylcarbamates afforded expected compounds (Table 3) and chloromethylphenyl *N*-methylcarbamates afforded under the equal conditions a mixture of compounds from which the product was not possible to be isolated by common laboratory procedures (distillation under reduced pressure, crystallization, separation on the column of SiO₂). By this reaction various solvents as propanone, acetonitrile, ethyl acetate, benzene, toluene, tetrahydrofuran, dioxan, and other as well as various reaction conditions were examined, however without a desired result. Therefore, a new route of preparation of alkylthiomethylphenols via the reaction of alkylthiomethylphenyl *N,N*-dimethylcarbamates with an aqueous sodium hydroxide was searched.

It was found that in dependence on the alkyl—S—CH₂ substituent it is also necessary to choose reaction conditions and the ratio of sodium hydroxide to carbamate.

Compounds containing a primary alkyl group reacted faster than those containing a secondary and tertiary groups, respectively. As concerns the position of the ethylthiomethyl group on the benzene ring, compounds having this group in position 4 on the benzene ring reacted faster than those with an ethylthiomethyl group in position 2 and 3.

The mass ratio of sodium hydroxide to carbamate was changed from 5:1 to 10:1 and the reaction time ranged from 3 to 18 h. A survey of alkylthiomethylphenols prepared is given in Table 4. From alkylthiomethylphenols prepared by this route appropriate *N*-methylcarbamates were prepared (Table 5).

Infrared spectra of alkylthiomethylphenyl *N*-methyl carbamates (Table 6) showed two absorption bands, $\nu(\text{NH})$, in the region of $\tilde{\nu} = 3365\text{—}3467\text{ cm}^{-1}$ assigning to the two various conformations of the CH₃—NH—CO group. In the infrared spectra of alkylthiomethylphenols (Table 7) an intense wide band in the region of $\tilde{\nu} = 3378\text{—}3400\text{ cm}^{-1}$ is observed ascribing to the vibration of the OH group involved in the intramolecular hydrogen bonding, $\nu(\text{OH}\dots\text{S})$, and a band of the free OH group, $\nu(\text{OH})$, in the region of $\tilde{\nu} = 3600\text{—}3577\text{ cm}^{-1}$.

When studying the pesticidal activity of the prepared compounds it was found that those in tests on herbicidal activity in examined concentrations were inactive. A measurable fungicidal activity against *E. graminis*, *E. polyphaga*, and *P. infestans* was observed only with compounds VII, XIX, and XXI, however, they did not reach the activity of the used standards (Table 8). Some compounds showed a contact insecticidal activity against *A. fabae*, where compounds XLVIII, XLIX, and LIII were equally or more active than the used standard malathion, by which

Table 2

Characterization of substituted phenyl *N*-methyl- or *N,N*-dimethylcarbamates

| Compound | R | R ¹ | X | w _i (calc.)/% w _i (found)/% | | | | Yield | M.p./°C |
|------------------|---|--|---|--|-----|------|------|-------|---------|
| | | | | C | H | N | S | % | |
| VII | H | CN | 2 | 54.0 | 4.5 | 12.6 | 14.4 | 79.2 | 61—62 |
| | | | | 54.1 | 4.6 | 12.5 | 14.6 | | |
| VIII | H | CN | 3 | 54.0 | 4.5 | 12.6 | 11.4 | 80.2 | 51—52 |
| | | | | 54.2 | 4.5 | 12.7 | 11.6 | | |
| IX | H | CN | 4 | 54.0 | 4.5 | 12.6 | 14.4 | 77.6 | 72—74 |
| | | | | 54.3 | 4.4 | 12.7 | 14.5 | | |
| X | H | C ₆ H ₅ | 2 | 65.9 | 5.5 | 5.1 | 11.7 | 80.0 | 103—105 |
| | | | | 66.0 | 5.6 | 5.0 | 11.9 | | |
| XI | H | C ₆ H ₅ | 3 | 65.9 | 5.5 | 5.1 | 11.7 | 84.0 | 90—91 |
| | | | | 66.1 | 5.5 | 5.0 | 11.8 | | |
| XII | H | C ₆ H ₅ | 4 | 65.9 | 5.5 | 5.1 | 11.7 | 80.9 | 82—84 |
| | | | | 65.8 | 5.4 | 5.2 | 11.9 | | |
| XIII | H | COC ₂ H ₅ S | 2 | 50.5 | 3.5 | 4.9 | 22.5 | 93 | 99—100 |
| | | | | 50.7 | 3.6 | 5.0 | 22.7 | | |
| XIV | H | COC ₂ H ₅ S | 3 | 50.5 | 3.5 | 4.9 | 22.5 | 88.4 | 81—83 |
| | | | | 50.4 | 3.4 | 5.1 | 22.6 | | |
| XV ^a | H | P(OCH ₃) ₂ S | 2 | — | — | 4.6 | 19.9 | 58.2 | — |
| | | | | — | — | 4.7 | 19.8 | | |
| XVI ^b | H | P(OCH ₃) ₂ S | 3 | — | — | 4.6 | 19.9 | 64.2 | — |
| | | | | — | — | 4.6 | 20.0 | | |
| XVII | H | CN(CH ₃) ₂ S | 2 | 50.7 | 5.7 | 8.8 | 22.5 | 88.6 | 102—104 |
| | | | | 50.9 | 5.8 | 9.9 | 22.4 | | |

Table 2 (Continued)

| Compound | R | R ¹ | X | $w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$ | | | | Yield | M.p./°C |
|--------------------|-----------------|--|---|--|-----|------|------|-------|---------|
| | | | | C | H | N | S | % | |
| XVIII | H | CN(CH ₃) ₂ S | 3 | 50.7 | 5.7 | 9.8 | 22.5 | 90.2 | 82-84 |
| | | | | 50.8 | 5.9 | 9.7 | 22.7 | | |
| XIX | CH ₃ | CN | 2 | 50.4 | 4.5 | 12.6 | 14.4 | 79.8 | 61-62 |
| | | | | 50.6 | 4.4 | 12.8 | 14.5 | | |
| XX | CH ₃ | CN | 3 | 50.4 | 4.5 | 12.6 | 14.4 | 80.9 | 58-59 |
| | | | | 50.5 | 4.6 | 12.7 | 14.6 | | |
| XXI | CH ₃ | CN | 4 | 50.4 | 4.5 | 12.6 | 14.4 | 76.2 | 60-62 |
| | | | | 50.6 | 4.5 | 12.8 | 14.3 | | |
| XXII ^c | CH ₃ | P(OCH ₃) ₂ S | 2 | — | — | 4.2 | 19.1 | 60.2 | — |
| | | | | — | — | 4.2 | 19.3 | | |
| XXIII ^d | CH ₃ | P(OCH ₃) ₂ S | 3 | — | — | 4.2 | 19.1 | 62.7 | — |
| | | | | — | — | 4.2 | 19.3 | | |

$w_i(\text{calc.})/w_i(\text{found})$: a) 9.6/9.7 % P; b) 9.6/9.5 % P; c) 9.2/9.3 % P; d) 9.2/9.4 % P.
X is the position of the CH₂SR¹ group on the benzene ring.

Table 3

Characterization of alkylthiomethylphenyl *N,N*-dimethylcarbamates

| Compound | R | R ¹ | X | w _i (calc.)/% w _i (found)/% | | | | Yield | B.p./°C(<i>p</i> /Pa) |
|----------|-----------------|--|---|--|-----|-----|------|-------|------------------------|
| | | | | C | H | N | S | % | |
| XXIV | CH ₃ | CH ₃ | 2 | 58.6 | 6.7 | 6.2 | 14.2 | 76.8 | 130(13) |
| | | | | 58.5 | 6.6 | 6.3 | 14.3 | | |
| XXV | CH ₃ | C ₂ H ₅ | 2 | 60.2 | 7.2 | 5.9 | 13.4 | 78.4 | 133(40) |
| | | | | 60.0 | 7.3 | 6.0 | 13.6 | | |
| XXVI | CH ₃ | C ₂ H ₅ | 3 | 60.2 | 7.2 | 5.9 | 13.4 | 95.0 | 135(26) |
| | | | | 60.4 | 7.4 | 5.8 | 13.5 | | |
| XXVII | CH ₃ | C ₂ H ₅ | 4 | 60.2 | 7.2 | 5.9 | 13.4 | 80.2 | — |
| | | | | 60.3 | 7.2 | 5.8 | 13.3 | | |
| XXVIII | CH ₃ | C ₃ H ₇ | 2 | 61.6 | 7.6 | 5.5 | 12.7 | 81.4 | 130(13) |
| | | | | 61.5 | 7.5 | 5.6 | 12.8 | | |
| XXIX | CH ₃ | CH(CH ₃) ₂ | 2 | 61.6 | 7.6 | 5.5 | 12.7 | 75.8 | 128(13) |
| | | | | 61.8 | 7.7 | 5.6 | 12.9 | | |
| XXX | CH ₃ | CH ₂ CH=CH ₂ | 2 | 62.1 | 6.8 | 5.6 | 12.8 | 76.6 | 129(13) |
| | | | | 62.2 | 6.8 | 5.7 | 12.9 | | |
| XXXI | CH ₃ | C ₄ H ₉ | 2 | 62.9 | 7.9 | 5.2 | 12.0 | 67.6 | 133(13) |
| | | | | 62.7 | 8.0 | 5.1 | 12.1 | | |
| XXXII | CH ₃ | CH ₂ CH(CH ₃) ₂ | 2 | 62.9 | 7.9 | 5.2 | 12.0 | 86.0 | 129(6.5) |
| | | | | 62.8 | 7.8 | 5.1 | 12.2 | | |
| XXXIII | CH ₃ | CH(CH ₃)C ₂ H ₅ | 2 | 62.9 | 7.9 | 5.2 | 12.0 | 80.3 | 126(6.5) |
| | | | | 63.0 | 8.0 | 5.1 | 12.1 | | |
| XXXIV | CH ₃ | C(CH ₃) ₃ | 2 | 62.9 | 7.9 | 5.2 | 12.0 | 61.9 | 127(13) |
| | | | | 63.1 | 7.9 | 5.1 | 12.1 | | |
| XXXV | CH ₃ | CH ₂ CH ₂ SC ₂ H ₅ | 2 | 56.2 | 7.1 | 4.7 | 21.4 | 85.4 | 153(13) |
| | | | | 56.0 | 7.0 | 4.8 | 21.5 | | |

Table 4

Characterization of alkylthiomethylphenols

| Compound | R ¹ | X | w _i (calc.)/% w _i (found)/% | | | Yield % | B.p./°C(p/Pa) M.p./°C |
|----------|--|---|--|-----|------|------------|--------------------------|
| | | | C | H | S | | |
| XXXVI | CH ₃ | 2 | 62.3 | 6.5 | 20.8 | 60.1 | 74—76(26) |
| | | | 62.4 | 6.4 | 21.0 | | |
| XXXVII | C ₂ H ₅ | 2 | 64.2 | 7.2 | 19.1 | 54.7 | 81—83(26) |
| | | | 64.3 | 7.3 | 19.3 | | |
| XXXVIII | C ₂ H ₅ | 3 | 64.2 | 7.2 | 19.1 | 60.3 | 100—102(13) |
| | | | 64.4 | 7.1 | 19.3 | | |
| XXXIX | C ₂ H ₅ | 4 | 64.2 | 7.2 | 19.1 | 50.2 | 114—116(52) |
| | | | 64.3 | 7.3 | 19.0 | | |
| XL | C ₃ H ₇ | 2 | 65.9 | 7.7 | 17.6 | 76.8 | 84—86(13) |
| | | | 66.0 | 7.6 | 17.8 | | |
| XLI | CH(CH ₃) ₂ | 2 | 65.9 | 7.7 | 17.6 | 80.2 | 80—81(6.5) |
| | | | 66.1 | 7.8 | 17.5 | | |
| XLII | CH ₂ CH=CH ₂ | 2 | 66.6 | 6.7 | 17.8 | 57.1 | 85—86(13) |
| | | | 66.8 | 6.8 | 17.9 | | |
| XLIII | C ₄ H ₉ | 2 | 67.3 | 8.2 | 16.3 | 47.2 | 96—98(13) |
| | | | 67.4 | 8.3 | 16.2 | | |
| XLIV | CH ₂ CH(CH ₃) ₂ | 2 | 67.3 | 8.2 | 16.3 | 56.3 | 104—106(42) |
| | | | 67.5 | 8.2 | 16.5 | | |
| XLV | CH(CH ₃)C ₂ H ₅ | 2 | 67.3 | 8.2 | 16.3 | 55.5 | 90—92(13) |
| | | | 67.2 | 8.3 | 16.4 | | |
| XLVI | C(CH ₃) ₃ | 2 | 67.3 | 8.2 | 16.3 | 73.8 | 69—70 |
| | | | 67.4 | 8.4 | 16.5 | | |
| XLVII | CH ₂ CH ₂ SC ₂ H ₅ | 2 | 57.9 | 7.1 | 28.0 | 86.5 | 141—143(26) |
| | | | 58.0 | 7.0 | 28.2 | | |

Table 5

Characterization of alkylthiomethylphenyl *N*-methylcarbamates

| Compound | R | R ¹ | X | w _i (calc.)/% w _i (found)/% | | | | Yield % | M.p./°C |
|----------|---|--|---|--|-----|-----|------|------------|---------|
| | | | | C | H | N | S | | |
| XLVIII | H | CH ₃ | 2 | 56.8 | 6.2 | 6.6 | 15.2 | 97.0 | 50—52 |
| | | | | 56.9 | 6.4 | 6.8 | 15.3 | | |
| XLIX | H | C ₂ H ₅ | 2 | 58.6 | 6.7 | 6.2 | 14.2 | 96.0 | 43—45 |
| | | | | 58.7 | 6.9 | 6.4 | 14.3 | | |
| L | H | C ₂ H ₅ | 3 | 58.6 | 6.7 | 6.2 | 14.2 | 98.0 | 44—46 |
| | | | | 58.5 | 6.8 | 6.3 | 14.5 | | |
| LI | H | C ₂ H ₅ | 4 | 58.6 | 6.7 | 6.2 | 14.2 | 96.0 | 91—93 |
| | | | | 58.7 | 6.8 | 6.1 | 14.4 | | |
| LII | H | C ₃ H ₇ | 2 | 60.2 | 7.2 | 5.9 | 13.4 | 98.0 | 60—62 |
| | | | | 60.1 | 7.3 | 6.0 | 13.3 | | |
| LIII | H | CH(CH ₃) ₂ | 2 | 60.2 | 7.2 | 5.9 | 13.4 | 97.0 | 66—68 |
| | | | | 60.3 | 7.4 | 5.9 | 13.5 | | |
| LIV | H | CH ₂ CH=CH ₂ | 2 | 60.7 | 6.4 | 5.9 | 13.5 | 98.0 | 37—40 |
| | | | | 60.6 | 6.3 | 5.8 | 13.2 | | |
| LV | H | C ₄ H ₉ | 2 | 61.6 | 7.6 | 5.5 | 12.7 | 96.0 | 34—36 |
| | | | | 61.7 | 7.7 | 5.4 | 12.9 | | |
| LVI | H | CH ₂ CH(CH ₃) ₂ | 2 | 61.6 | 7.6 | 5.5 | 12.7 | 95.0 | 59—61 |
| | | | | 61.5 | 7.7 | 5.6 | 12.9 | | |
| LVII | H | CH(CH ₃)C ₂ H ₅ | 2 | 61.6 | 7.6 | 5.5 | 12.7 | 94.0 | 44—46 |
| | | | | 61.8 | 7.7 | 5.5 | 12.6 | | |
| LVIII | H | C(CH ₃) ₃ | 2 | 61.6 | 7.6 | 5.5 | 12.7 | 91.0 | 83—85 |
| | | | | 61.4 | 7.5 | 5.4 | 12.6 | | |
| LIX | H | CH ₂ CH ₂ SC ₂ H ₅ | 2 | 54.7 | 6.7 | 4.9 | 22.5 | 97.0 | 29—31 |
| | | | | 54.8 | 6.8 | 4.8 | 22.7 | | |

Table 6

Infrared spectral data of compounds studied

| Compound | $\bar{\nu}_i(\text{CHCl}_3\text{---CCl}_4)/\text{cm}^{-1}$ | | | | |
|----------|--|-------------------|-------------------|-------------------|-------------------|
| | $\nu(\text{C=O})$ | $\nu(\text{C—O})$ | $\nu(\text{SCN})$ | $\nu(\text{C—N})$ | $\nu(\text{N—H})$ |
| I | 1742 | 1150 | — | 1483 | 3462 |
| II | 1740 | 1152 | — | 1484 | 3460 |
| III | 1740 | 1152 | — | 1483 | 3461 |
| IV | 1716 | 1156 | — | 1382 | — |
| | 1726 | 1155 | — | 1384 | — |
| V | 1702 | 1164 | — | 1381 | — |
| | 1712 | 1163 | — | 1380 | — |
| VI | 1713 | 1164 | — | 1372 | — |
| | 1721 | 1164 | — | 1378 | — |
| VII | 1742 | 1180 | 2156 | 1487 | 3454 |
| VIII | 1740 | 1152 | 2156 | 1488 | 3452 |
| IX | 1741 | 1160 | 2160 | 1486 | 3453 |
| X | 1742 | 1175 | — | 1482 | 3460 |
| XI | 1743 | 1172 | — | 1484 | 3461 |
| XII | 1744 | 1176 | — | 1482 | 3460 |
| XIX | 1718 | 1162 | 2150 | 1388 | — |
| XX | 1720 | 1166 | 2152 | 1390 | — |
| XXI | 1719 | 1164 | 2151 | 1386 | — |
| XXIV | 1716 | 1163 | — | 1387 | — |
| | 1723 | 1160 | — | — | — |
| XXV | 1721 | 1172 | — | 1384 | — |
| XXVI | 1724 | 1168 | — | 1388 | — |
| XXVII | 1722 | 1166 | — | 1387 | — |
| XXVIII | 1724 | 1171 | — | 1391 | — |
| XXIX | 1722 | 1170 | — | 1393 | — |
| XXX | 1724 | 1167 | — | 1390 | — |
| XXXI | 1726 | 1168 | — | 1392 | — |
| XXXII | 1724 | 1158 | — | 1381 | — |
| XXXIII | 1719 | 1156 | — | 1387 | — |
| XXXIV | 1717 | 1154 | — | 1381 | — |
| XXXV | 1727 | 1162 | — | 1387 | — |
| XLVIII | 1737 | 1171 | — | 1423 | 3457 |
| | | | | | 3360 |
| XLIX | 1748 | 1176 | — | 1482 | 3467 |
| | | | | | 3358 |
| L | 1734 | 1150 | — | 1480 | 3463 |
| | | | | | 3365 |
| LI | 1729 | 1190 | — | 1495 | 3460 |
| | | | | | 3353 |
| LII | 1729 | 1171 | — | 1478 | 3454 |
| | | | | | 3351 |

Table 6 (Continued)

| Compound | $\bar{\nu}_i(\text{CHCl}_3\text{—CCl}_4)/\text{cm}^{-1}$ | | | | |
|--------------|--|-------------------|-------------------|-------------------|-------------------|
| | $\nu(\text{C=O})$ | $\nu(\text{C—O})$ | $\nu(\text{SCN})$ | $\nu(\text{C—N})$ | $\nu(\text{N—H})$ |
| <i>LIII</i> | 1738 | 1177 | — | 1483 | 3460 3361 |
| <i>LIV</i> | 1740 | 1175 | — | 1483 | 3459 3357 |
| <i>LV</i> | 1741 | 1182 | — | 1483 | 3463 3362 |
| <i>LVI</i> | 1739 | 1176 | — | 1484 | 3466 3350 |
| <i>LVII</i> | 1733 | 1174 | — | 1475 | 3457 3358 |
| <i>LVIII</i> | 1749 | 1173 | — | 1478 | 3466 3360 |
| <i>LIX</i> | 1741 | 1178 | — | 1483 | 3465 3350 |

Table 7

Infrared spectral data of alkylthiomethylphenols

| Compound | $\bar{\nu}_i(\text{CHCl}_3\text{—CCl}_4)/\text{cm}^{-1}$ | | | | |
|----------------|--|----------------------|-------------------|-----------------------|-------------------|
| | $\nu(\text{O—H})$ | $\nu(\text{OH...S})$ | $\nu(\text{C=C})$ | $\delta(\text{CH}_3)$ | $\nu(\text{C—O})$ |
| <i>XXXVI</i> | 3585 3600 | 3303 3320 | 1576 1574 | 1476 1471 | 1226 1229 |
| <i>XXXVII</i> | 3583 3600 | 3300 3324 | 1577 1573 | 1449 1447 | 1227 1229 |
| <i>XXXVIII</i> | 3583 3600 | 3329 3340 | 1584 1585 | 1448 1449 | 1269 1270 |
| <i>XXXIX</i> | 3588 3600 | 3340 3378 | 1601 1591 | 1436 1436 | 1256 1254 |
| <i>XL</i> | 3583 3600 | 3314 3324 | 1573 1579 | 1478 1480 | 1227 1216 |
| <i>XLI</i> | 3382 3600 | 3321 3324 | 1576 1579 | 1478 1481 | 1226 1217 |
| <i>XLII</i> | 3584 3600 | 3316 3344 | 1577 1577 | 1478 1481 | 1228 1217 |
| <i>XLIII</i> | 3577 3600 | 3300 3302 | 1574 1570 | 1477 1478 | 1229 1216 |
| <i>XLIV</i> | 3593 3600 | 3302 3326 | 1578 1578 | 1482 1482 | 1226 1232 |

Table 7 (Continued)

| Compound | $\bar{\nu}_i(\text{CHCl}_3\text{---CCl}_4)/\text{cm}^{-1}$ | | | | |
|----------|--|----------------------|--------------------------|-----------------------|---------------------|
| | $\nu(\text{O---H})$ | $\nu(\text{OH...S})$ | $\nu(\text{C}=\text{C})$ | $\delta(\text{CH}_3)$ | $\nu(\text{C---O})$ |
| XLV | 3585 | 3300 | 1576 | 1478 | 1226 |
| | 3600 | 3300 | 1570 | 1472 | 1231 |
| XLVI | 3584 | 3316 | 1573 | 1478 | 1226 |
| | 3600 | 3329 | 1576 | 1482 | 1226 |
| XLVII | 3590 | 3329 | 1577 | 1478 | 1231 |
| | 3600 | 3341 | 1577 | 1479 | 1236 |

Table 8

Fungicidal activity of some compounds

| Compound | ED ₅₀ /ppm | | |
|--------------------|-----------------------|--------------------|---------------------|
| | <i>P. infestans</i> | <i>E. graminis</i> | <i>E. polyphaga</i> |
| VII | — | 120.0 | 95.5 |
| XIX | — | 1000.0 | 83.5 |
| XXI | 380 | 38.5 | 3650.0 |
| dinocap — standard | — | 24.5 | 3.16 |
| mancozeb | 73 | — | — |

the most active compound *N*-methyl-*O*-(2-isopropylthiomethyl)phenyl carbamate *LIII* was 2.8 times more active than a standard. The activity of the standard was reached also by compounds *XXIV*, *XXV*, *XXIX*, *L*, and *LII*. In systemic insecticidal activity against *M. sanbornii* only compounds *XLVIII* and *XLIX* were 2.5 to 3 times more active than the used standard thiometon. From the remaining compounds only compound *XXIV* was interesting. Some compounds showed a measurable acaricidal activity against *T. urticae*, however, none of them showed interesting activity (Table 9). In other tests on *M. domestica*, *S. granarius*, and *T. urticae* compounds in concentrations used were practically inactive.

Summarising it can be stated that the most active were compounds *N*-methyl-*O*-(2-methylthiomethyl)phenyl carbamate *XLVIII* and *N*-methyl-*O*-(2-ethylthiomethyl)phenyl carbamate *XLIX* and there is no large difference in activity of these compounds. In contact insecticidal tests an interesting activity showed

Table 9

Insecticidal and acaricidal activities of some prepared compounds

| Compound | LC ₅₀ /% | | |
|-----------------|---------------------|-----------------------|-------------------|
| | <i>A. fabae</i> | <i>M. sanbornii</i> * | <i>T. urticae</i> |
| VII | 0.06 | 0.5 | 0.5 |
| VIII | 0.07 | 0.5 | 0.5 |
| IX | 0.06 | 0.5 | 0.5 |
| X | 0.08 | 0.5 | 0.5 |
| XI | 0.04 | 0.5 | 0.01 |
| XII | 0.05 | 0.5 | 0.5 |
| XIII | 0.05 | 0.5 | 0.10 |
| XV | 0.05 | 0.40 | 0.01 |
| XXII | 0.07 | 0.30 | 0.1 |
| XXIV | 0.00195 | 0.051 | 0.10 |
| XXV | 0.0033 | 0.5 | 0.1 |
| XXVI | 0.08 | 0.5 | 0.1 |
| XXVIII | 0.01 | 0.5 | 0.1 |
| XXIX | 0.0036 | 0.5 | 0.1 |
| XXX | 0.01 | 0.5 | 0.1 |
| XXXI | 0.04 | 0.5 | 0.1 |
| XXXII | 0.01 | 0.5 | 0.1 |
| XXXIII | 0.03 | 0.5 | 0.1 |
| XXXIV | 0.012 | 0.5 | 0.1 |
| XXXV | 0.010 | 0.5 | 0.10 |
| XLVIII | 0.0016 | 0.007 | 0.10 |
| XLIX | 0.0013 | 0.0052 | 0.025 |
| L | 0.0096 | 0.40 | 0.010 |
| LI | 0.1 | 0.5 | 0.05 |
| LII | 0.0036 | 0.5 | 0.1 |
| LIII | 0.00057 | 0.5 | 0.1 |
| LIV | 0.010 | 0.5 | 0.04 |
| LVI | 0.010 | 0.08 | 0.05 |
| LIX | 0.03 | 0.5 | 0.1 |
| malathion | 0.0016 | — | — |
| thiometon | — | 0.0178 | — |
| carbophenothion | — | — | 0.0003 |

* Systemic activity.

2-(isopropylthiomethyl)phenyl *N*-methylcarbamate *LIII*. From the practical point of view compound *XLVIII* was very interesting, however from the technical-ecological point of view it has a disadvantage in the use of methanethiol.

Experimental

Infrared spectra of compounds prepared were recorded with a UR-20 (Zeiss, Jena) instrument. The wavenumber calibration was checked against the spectrum of polystyrene. The spectra were recorded in trichloromethane and some of them in tetrachloromethane ($c = 20\text{--}60 \text{ mmol dm}^{-3}$, cell thickness 0.89 mm).

Fungicidal activity of the prepared compounds was tested by both the *in vitro* and *in vivo* methods. Inherent activity was investigated by the glass slide method on spores of fungi *Sclerotinia fructicola* (WINT.) and by the Sharvell method using captan (trichloromethylthio)-4-cyclohexene-1,2-dicarboximide as standard on *Aspergillus niger* TIEGH. and *Cladosporium cucumericum* ELL. et ARTH. Antipowdery mildew activity was followed on *Erysiphe graminis* (on the living plants of spring barley, sort Dunajský trh) using dinocap (2-(1-methylheptyl)-4,6-dinitrophenyl (E)-2-butenate) as standard and on tomatoes (*Phytophthora infestans* DE BY) using mancozeb (a mixture of manganese(II) and zinc(II) 1,2-ethanediybis(carbamodithioates)) as standard according to the known methods [3].

The mordant activity was determined on dead caryopsis of rye infected by conidia of *Fusarium nivale* using dithiocyanomethane as standard after the known methods [4].

Herbicidal activity was investigated by the preemergent (into the soil) and postemergent (to the leaf) application methods using testing objects: *Avena sativa* L., *Polygonum persicaria* L., *Fagopyrum sagittatum* L., and *Sinapis alba* L. after the known methods [5].

According to previously published methods [3, 6] the prepared compounds were tested on contact insecticidal activity on *Musca domestica*, *Sitophilus granarius*, and *Aphis fabae* SCOP using fenitrothion (*O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl)thiophosphate) as standard; on systemic insecticidal activity on *Macrosiphoniella sanbornii* THEOB., on *Chrysanthemum indicum* using thiomethon (*S*-[2-(ethylthio)ethyl] *O,O*-dimethyl dithiophosphate) as standard; on acaricidal activity on females *Tetranychus urticae* KOCH and on ovicidal activity on eggs of *T. urticae*) using carbophenothion (*S*-[(4-chlorophenyl)thiomethyl] *O,O*-diethyl dithiophosphate) as standard.

Cresyl chlorocarbonates

To cresol (3.38 mol) and *N,N*-dimethylaniline (3.38 mol) in toluene (600 cm³) fosgene (3.4 mol) dissolved in toluene (400 cm³) was added with stirring at -5 to 0 °C during 2 h. Then the reaction mixture was stirred at the same temperature for 1 h and at $15\text{--}20$ °C for 2 h. The excluded *N,N*-dimethylanilinium chloride was separated by filtration and washed with toluene on the filter. Combined toluene filtrates were concentrated under reduced pressure and the rest was redistilled.

2-Methylphenyl chlorocarbonate: b.p. = 88 °C at 1.3 Pa, yield = 77.8 %; 3-methylphenyl chlorocarbonate: b.p. = 93 °C at 1.6 Pa, yield = 81.3 %; 4-methylphenyl chlorocarbonate: b.p. = 91 °C at 1.3 Pa, yield = 79.4 %.

Chloromethylphenyl chlorocarbonates

To methylphenyl chlorocarbonate (2.03 mol), phosphorus trichloride (0.049 mol), and benzamide (0.00576 mol) suluryl chloride (2.46 mol) was slowly added with stirring at 130 to 135 °C during 5 h. During addition hydrogen chloride and sulfur dioxide evolved. After cooling the reaction mixture was filtered and distilled under diminished pressure.

2-(Chloromethyl)phenyl chlorocarbonate: b.p. = 71—74 °C at 13.3 Pa, yield = 50.1 % ;
3-(chloromethyl)phenyl chlorocarbonate: b.p. = 81—82 °C at 26.6 Pa, yield = 48.2 % ;
4-(chloromethyl)phenyl chlorocarbonate: b.p. = 73—75 °C at 13.3 Pa, yield = 49.0 %.

(Chloromethyl)phenyl N-methyl- or N,N-dimethylcarbamates (I—VI)

To (chloromethyl)phenyl chlorocarbonate (1 mol) in 1,1,2-trichloroethene (300 cm³) methylamine and dimethylamine was introduced under the level of the solution during 2 h at –5 to 5 °C with stirring. After addition the stirring was continued at 10 to 15 °C for 30 min. The reaction mixture was poured into ice water (1200 cm³) under stirring. The organic layer was washed with water (300 cm³) and dried with anhydrous CaCl₂. After distillation of 1,1,2-trichloroethene the rest was purified by crystallization from cyclohexane or by distillation under reduced pressure (Table 1).

Substituted phenyl N-methyl- or N,N-dimethylcarbamates (VII—XXIII)

To (chloromethyl)phenyl *N*-methyl- or *N,N*-dimethylcarbamate (0.1 mol) in acetonitrile (100 cm³) potassium rhodanide, sodium thiophenolate, sodium *O*-ethylxantogenate, sodium *N,N*-dimethyldithiocarbamide or sodium salt of *O,O*-dimethyldithiophosphoric acid (0.11 mol) was added under stirring. The stirring was continued for 2 to 4 h at the boiling point of the reaction mixture. After cooling the reaction mixture was poured into water (500 cm³) under stirring by which a solid or an oily compound was excluded. The solid compound was purified by crystallization from cyclohexane, toluene or ethanol. In the case of the oily compound toluene (150 cm³) was added, the mixture was dried over anhydrous sodium sulfate, toluene was distilled off under reduced pressure and the rest was dried at 80 °C at 13.3 Pa (Table 2).

Alkylthiomethylphenyl N,N-dimethylcarbamates (XXIV—XXXV)

To (chloromethyl)phenyl *N,N*-dimethylcarbamate (0.1 mol) in acetonitrile (100 cm³), sodium thiolate (0.11 mol) as a suspension in toluene (100 cm³) was added. The reaction mixture was stirred under reflux for 2 h and after cooling washed with water (twice with 200 cm³) and with sodium carbonate (100 cm³ of 5 % solution). After drying over anhydrous sodium sulfate toluene was distilled off under reduced pressure and the rest was distilled (Table 3).

Alkylthiomethylphenols (XXXVI—XLVII)

After dissolving sodium hydroxide (0.745 to 1.49 mol) in water (120 cm³) alkylthio-*methylphenyl N,N*-dimethylcarbamate (0.149 mol) was added. The reaction mixture was

maintained at a boiling point for 3 to 18 h until the solution was clear. The reaction mixture was acidified (pH = 1) by hydrochloric acid (15 %). The excluded alkylthiomethylphenol was extracted with toluene (120 cm³). After drying over anhydrous sodium sulfate toluene was distilled off under reduced pressure and the rest was distilled (Table 4).

Alkylthiomethylphenyl N-methylcarbamates (XLVIII—LIX)

To alkylthiomethylphenol (0.1 mol) and triethylamine (0.5 cm³) in benzene (100 cm³) methylisothiocyanate (0.11 mol) in benzene (30 cm³) was added at 10 to 15 °C under stirring. The stirring was continued for 1 h at 40 °C and for 1 h at 80 °C. Benzene was distilled off under reduced pressure and at the end of distillation at 80 °C at 13.3 Pa and the rest was purified by crystallization from hexane (Table 5).

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