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Note

2-Bromo-1-ethoxy-(2′,4′-dichloro)styrene and 2,2-dibromo-1-ethoxy-(2′,4′-dichloro)styrene—the two impurities of bromfenvinphos; their identification, synthesis and full characterization

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Insecticide bromfenvinphos of 94–96% purity is manufactured in the Institute of Industrial Organic Chemistry. Besides the main component (bromfenvinphos), more than ten impurities are observed. Two new impurities: 2-bromo-1-ethoxy-(2′,4′-dichloro)styrene (as a mixture of geometric isomers) and 2,2-dibromo-1-ethoxy-(2′,4′-dichloro)styrene were identified by means of mass spectrometry (MS) analysis. Both impurities were independently synthesized using 2,4-dichloroacetophenone as the starting material. The synthesized compounds were characterized spectroscopically and were found identical to the impurities which had been previously identified in bromfenvinphos.

Keywords: bromfenvinphos, impurities, mass spectrometry.

Introduction

Bromfenvinphos (Fig. 1) is a known, original insecticide with varroacidal activity.[1–4] Methods concerning its synthesis and process of manufacturing,[5–7] knowledge about its biological activity,[8–13] as well as determination of its residues in the environment[14–17] have been developed in the Institute of the Industrial Organic Chemistry since the beginning of 1970s.

Bromfenvinphos of 94–96% purity is manufactured in the Institute of Industrial Organic Chemistry. Besides the main component (bromfenvinphos), more than ten impurities are observed.[18–20] Because the impurities of the manufactured bromfenvinphos should be fully, unambiguously and completely characterized, herein we present the identification and independent synthesis of two, so-far uncharacterized, impurities.

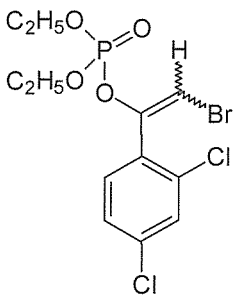

Fig. 1. (*E*,*Z*)-*O*,*O*-Diethyl-*O*-[1-(2,4-dichlorophenyl)-2-bromovinyl] phosphate, bromfenvinphos.

Materials and Methods

1. General

All reagents were commercially available and were used as received without further purification. The reaction progress was monitored by means of TLC: silica gel: Merck Alufolien 5554; visualization: UV 254 nm and/or 1% ethanolic $AgNO_3$/UV; mobile phases: hexane : benzene 1 : 1 (v/v) (for **1**,**4**), hexane:benzene 3 : 2 (v/v) (for **2**,**5**). Column chromatography: silica gel Merck 7734, 70–230 mesh, mobile phase: hexane. Refractive index values were measured with an Abbe refractometer (Carl Zeiss/Jena). GC/MS were recorded using a gas chromatograph (6890N Series Network GC System; Agilent Technologies) equipped with a DB-5MS capillary column 30 m×0.25 mm, film thickness 0.25 μm, column temperature starting at 100°C (3 min.) and increased to 250°C (10°C/min.), and an injector (split/splitless 20 : 1), temperature 240°C. Helium was used as a carrier gas; 500 to 1000 ng of the analyzed substance was introduced into the injector in 0.2 μl of hexane solution. EI MS (70 eV) and CI MS (isobutane) (*m*/*z*, int. [%]) were recorded using a mass detector (MSD 5975B series; Agilent Technologies) (ion source temperature: 230°C) spectrometer. ^{1}H NMR data (200 MHz or 500 MHz, δ_H [ppm], *J* [Hz], $CDCl_3$, TMS as a standard) were recorded using a spectrometer (UNITYplus 200 or UNITYplus 500; Varian, respectively). ^{13}C NMR data (50 MHz, δ_C [ppm], *J* [Hz], $CDCl_3$, TMS as a standard) were recorded using a spectrometer (UNITYplus 200; Varian). IR (ν [cm^{-1}]) data were recorded using a FT/IR spectrophotometer (420; Jasco).

2. Synthesis of the compounds

2.1. 2,4-Dichlorophenacyl bromide (4)

2,4-Dichloracetophenone (**3**) (113.4 g, 0.6 mol) and carbon tetrachloride (360 ml) were placed in a reactor of 750 ml capacity, equipped with a heating mantle, mechanical stirrer, dropping funnel, thermometer, and reflux condenser with a hydrogen bromide

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absorber. Bromine (96 g, 0.6 mol) was added dropwise at 35–40°C for 1 hr, at such a rate to keep the reaction mixture colorless. Stirring was continued at 40°C for 2 hr. The reaction mixture was washed with 5% sodium bisulfite (180 ml), twice with water, and dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure, and the residue was distilled (103–106°C/0.4 mmHg) to give crude 2,4-dichlorophenacyl bromide (**4**) (108 g, 67%, n_D^{30} 1.6018). The crude **4** (108 g) and hexane (300 ml) were placed in a reactor of 750 ml capacity at 25–30°C and kept at this temperature for 1 hr. The solution was slowly cooled to 0°C and stirred at 0°C for 1 hr. After filtration and drying in a dessicator, purified 2,4-dichlorophenacyl bromide (**4**) (89.3 g) was obtained. The crystallization process was repeated to afford 2,4-dichlorophenacyl bromide (**4**) as a certified reference material of min. 99.8% purity (HPLC, GC, TLC): 69.9 g, 44%, m.p. 23–24°C (23–24°C,[20] 25–29°C,[21] 30–32°C[22]).

2.2. *2,4-Dichlorophenacyl bromide diethyl ketal (5)*

2,4-Dichlorophenacyl bromide (**4**) (26.8 g, 0.1 mol), triethyl orthoformate (25 ml, 22.3 g, 0.15 mol), anhydrous ethanol (53.5 ml) and Nafion NR 50 (1.5 g) were placed in a round-bottomed flask. The reaction mixture was stirred and heated at boiling point for 14 hr. The progress of the reaction was monitored by TLC. After the reaction had been finished, the reaction mixture was alkalized with 5% sodium ethoxide to pH 7. The formed precipitate was filtered off, and the filtrate was concentrated to dryness to give 26.6 g of the residue, which was purified by column chromatography to give 2,4-dichlorophenacyl bromide diethyl ketal (**5**) as a colorless oil: 9.6 g, 28%; purity: 98.7% (GC), n_D^{25} 1.5209.

EI GC/MS; retention time: 13.893 min, 99.0% (internal standardization): 299 (13), 297 (30), 295 (19, M-OEt), 271 (19), 269 (43), 267 (27), 249 (64), 247 (100), 221 (15), 219 (24), 193 (48), 191 (77), 175 (49), 173 (79), 161 (17), 159 (29).

^{1}H NMR δ_H (200 MHz, $CDCl_3$): 1.27 (t, 6H, J=7.0 Hz, CH_3), 3.3–3.6 (m, 4H, 2(OCH_2CH_3), 3.93 (s, 2H, CH_2Br), 7.32 (dd, 1H, J=2.1, 8.5 Hz, H_{ar}), 7.39 (d, 1H, J=2.1 Hz, H_{ar}), 7.85 (d, 1H, J=8.5 Hz, H_{ar}).

^{13}C NMR δ_C (50 MHz, $CDCl_3$): 15.2, 32.5, 57.4, 100.1, 126.7, 130.8, 132.1 133.5, 134.5, 135.1.

IR (film): 2977, 2920, 2890, 1586, 1557, 1468, 1376, 1268, 1054, 823, 636.

2.3. *2-Bromo-1-ethoxy-(2′,4′-dichloro)styrene (1) (a sum of isomers)*

2,4-Dichlorophenacyl bromide diethyl ketal (**5**) (13.1 g; 0.038 mol) was placed in a flask of 250 ml capacity equipped with a distillation condenser. Xylene (mixture of isomers, 60 ml) and a catalyst, Nafion NR50 (0.15 g) were added. The mixture of xylene and ethanol was slowly distilled off. Simultaneously, additional xylene (100 ml) was added dropwise into the distillation flask from a dropping funnel placed on the top of a distillation adapter. Overall, 153 ml of the mixture of xylene and ethanol were distilled off. The residue contained 36% of the product (GC) was diluted with chloroform (20 ml) and placed in a separation funnel. The chloroform layer was washed with 5% sodium carbonate solution (15 ml), water (2×15 ml), dried with anhydrous magnesium sulfate, filtered, and concentrated to dryness to afford the crude product (11.3 g), which was subjected to column chromatography to give 2-bromo-1-ethoxy-(2′,4′-dichloro)styrene (**1**) as a colorless oil: 9.212 g, 82%, n_D^{26} 1.5734, purity 98.2% (GC, isomer ratio: 42.9% : 55.2%), content of the starting ketal **5**: 1.4%.

EI GC/MS; retention time: 12.616 min (43.1%), 12.916 min (55.2%) (internal standardization); the same mass spectrum for both isomers: 298 (28), 296 (62), 294 (43, M), 270 (46), 268 (100), 266 (62), 241 (9), 237 (13), 189 (34), 187 (52), 175 (50), 173 (95), 171 (42), 161 (30), 159 (47), 148 (21), 146 (32), 136 (14), 135 (15), 125 (25), 123 (76), 111 (11), 109 (20), 99 (21), 75 (21), 74 (22).

^{1}H NMR δ_H (500 MHz, sum of isomers, $CDCl_3$): 1.26 (t, 3H, J=7.0 Hz, $OCH_2\mathbf{CH_3}$), 1.35 (t, 3H, J=7.0 Hz, $OCH_2\mathbf{CH_3}$), 3.69 (q, 2H, J=7.0 Hz, $OCH_2\mathbf{CH_3}$), 3.90 (q, 2H, J=7.0 Hz, OCH_2CH_3), 5.56 (s, 1H, CHBr), 5.59 (s, 1H, CHBr), 7.24–7.31 (m, 4H, H_{ar}), 7.42–7.45 (m, 2H, H_{ar}).

^{13}C NMR δ_C (50 MHz, sum of isomers, $CDCl_3$): 14.6, 15.4, 64.9, 65.6, 82.8, 90.1, 127.2, 127.4, 129.8, 130.1, 131.6, 131.8, 132.1, 132.2, 133.5, 134.4, 135.6, 136.0, 153.3, 155.3.

IR (sum of isomers, film): 2981, 1625, 1584, 1470, 1377, 1305, 1187, 1130, 1102, 1052.

2.4. *2,2-Dibromo-1-ethoxy-(2′,4′-dichloro)styrene (2)*

2-Bromo-1-ethoxy-(2′,4′-dichloro)styrene (**1**) (0.760 g, 0.0026 mol) in methylene chloride (2 ml) was placed in a reactor equipped with a magnetic stirring bar, reflux condenser, dropping funnel, thermometer, and hydrogen bromide absorber. The solution of bromine (0.41 g, 0.129 ml) in methylene chloride (3.2 ml) was added dropwise at 0°C at such a rate to maintain a colorless solution. After all the bromine solution had been added, the temperature of the reaction mixture was increased to 10°C and triethylamine (0.44 g, 0.6 ml, 0.004 mol) was added dropwise. The temperature of the reaction mixture rose violently to 45°C, the solution was stirred for 0.5 hr, and then was left for 48 hr at room temperature. Hexane (10 ml) was added to the solution, and the formed precipitate was filtered off. The filtrate was concentrated to dryness to afford a dark residue (0.934 g), which was subjected to column chromatography to give 2,2-dibromo-1-ethoxy-(2′,4′-dichloro)styrene (**2**) as a colorless oil: 0.551 g, n_D^{25} 1.5925, purity 89.5% (GC), content of the 2-bromo-1-ethoxy-(2′,4′-dichloro)styrene (**1**), only one isomer: 9%. Yield of 2: 50.6%.

EI GC/MS; retention time: 14.556 min, 89.5% (internal standardization): 378 (14), 376 (41), 374 (45), 372 (18, M), 350 (31), 348 (88), 346 (100), 344 (40), 319 (7), 317 (8), 269 (10), 267 (23), 265 (14), 250 (15), 248 (10), 241 (13), 239 (29), 237 (19), 202 (24), 200 (47), 198 (23), 175 (55), 173 (85), 159 (39), 157 (57), 147 (26), 145 (40), 123 (20), 109 (30), 99 (13), 98 (15), 87 (21), 75 (20), 74 (22), 73 (13).

^{1}H NMR δ_H (200 MHz, $CDCl_3$): 1.26 (t, 6H, J=7.0 Hz, CH_3), 3.63 (q, 1H, J=7.0 Hz, OCH_2), 7.28 (d, 1H, J=8.5 Hz, H_{ar}), 7.32 (dd, 1H, J=2.0, 8.5 Hz, H_{ar}), 7.48 (d, 1H, J=2.0 Hz, H_{ar}).

^{13}C NMR δ_C (50 MHz, $CDCl_3$): 15.3, 66.3, 78.9, 127.4, 129.9, 131.1, 132.1, 134.8, 136.3, 151.4.

IR (film): 2981, 1583, 1469, 1377, 1284, 1241, 1108, 1054.

Results and Discussion

Bromfenvinphos manufactured in the Institute of Industrial Organic Chemistry was analyzed by both electron ionization mass spectrometry (EI GC/MS) and chemical ionization mass spectrometry (CI GC/MS).

GC peaks were attributed to the main component, bromfenvinphos and the known impurities were recognized. Besides the above mentioned peaks, three new signals were identified. The following retention times were found: τ_1=12.6 min (0.04%), τ_2=12.9 min (0.32%) and τ_3=14.5 min (0.15%) (Fig. 2).

The impurity, which is characterized by a peak retention time of τ_2=12.9 min (EI GC/MS) exhibits a molecular peak at *m/z*=294 and an isotope profile corresponding to 2Cl and 1Br. The peak retention time of τ_3=14.5 min (EI GC/MS) exhibits a molecular peak at *m/z*=372 and an isotope profile corresponding to 2Cl and 2Br. Analysis of both peaks (τ_2, τ_3) by CI GC/MS confirmed that the respecive signals $[M+1]^+$ ions at *m/z* 295 and *m/z* 373 correspond to the recognized molecular ions 294 and 372. Analysis of the impurity, which is characterized by the peak retention time of τ_1=12.6 min (CI GC/MS) exhibits a signal at $[M+1]^+$ ion at *m/z* 295 and an isotope profile similar to 2Cl and 1Br (analogous to the peak retention time of τ_2=12.9 min), which corresponds to molecular mass 294.

The following fragmentation pathways for the signals characterized by the peak retention times of τ_2=12.9 min and τ_3=14.5 min (EI GC/MS) are proposed (Eqs. 1, 2).

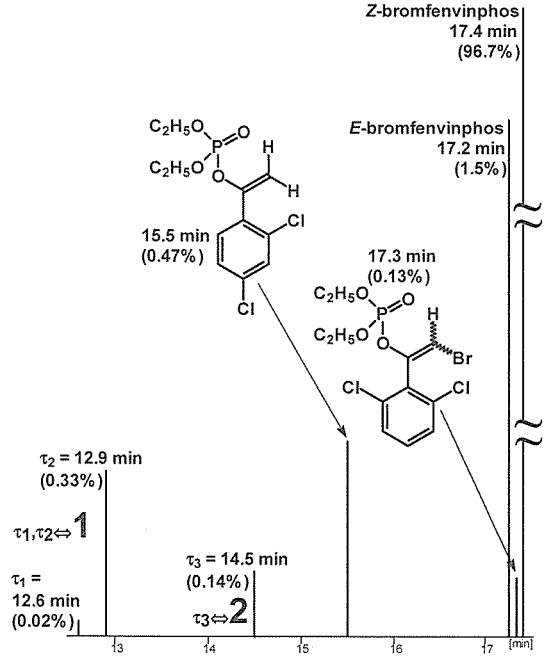

Fig. 2. Part of the GC/MS chromatogram of bromfenvinphos.

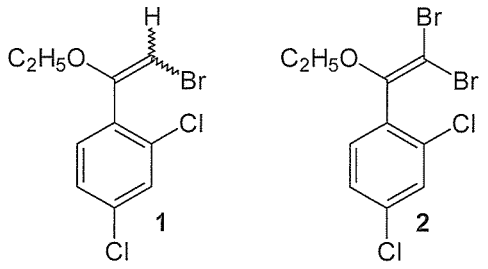

Fig. 3. Structures of 2-bromo-1-ethoxy-(2′,4′-dichloro)styrene (**1**⇔τ_1, τ_2), two geometric isomers and 2,2-dibromo-1-ethoxy-(2′,4′-dichloro)styrene (**2**⇔τ_3).

$$M^{+\bullet}\ m/z\ 294,\ 2Cl\ \text{and}\ 1Br \xrightarrow[-C_2H_4]{-28} m/z\ 266,$$

$$2Cl\ \text{and}\ 1Br \xrightarrow[-Br^{\bullet}]{-79} m/z\ 187,\ 2Cl \qquad (1)$$

and

$$M^{+\bullet}\ m/z\ 372,\ 2Cl\ \text{and}\ 1Br \xrightarrow[-C_2H_4]{-28} m/z\ 344,$$

$$2Cl\ \text{and}\ 2Br \xrightarrow[-Br^{\bullet}]{-79} m/z\ 265,\ 2Cl\ \text{and}\ 1Br \qquad (2)$$

For both signals (τ_2 and τ_3) the characteristic acyl fragment at *m/z* 173 ($2,4\text{-}Cl_2C_6H_3C{\equiv}O^+$) was recognized. The presented characteristic fragments suggested the following structure for both impurities: 2-bromo-1-ethoxy-(2′,4′-dichloro)styrene (**1**⇔τ_1, τ_2) and 2,2-dibromo-1-ethoxy-(2′,4′-dichloro)styrene (**2**⇔τ_3) (Fig. 3).

The expected *O,O*-dialkyl-*O*-[1-(2,4-dichlorophenyl)]-2-bromovinyl phosphates are the products of the Perkow reaction[23] between trialkyl phosphites and 2,4-dichlorophenacylidene bromide. Besides the expected main product, compounds with two bromine atoms, without bromine at all, and compounds with *alfa*-alkoxy substituent and 2,4-dichlorophenacyl bromide are present.[20] The authors propose the formation mechanism of the above products (including **1** and **2**). The following ion pairs are suspected to play a key role in the formation of **1** and **2** (Fig. 4).

The best way to confirm the structure of any compound being identified is to synthesize it and to compare its properties with an analyzed compound. We therefore independently synthesized the investigated impurities **1** and **2**; however, although the syntheses of 2-bromo-1-methoxy-(2′,4′-dichloro)styrene and 2,2-dibromo-1-methoxy-(2′,4′-dichloro)styrene were succesful,[20] attempts by the same authors to synthesize 2-bromo-1-ethoxy-(2′,4′-

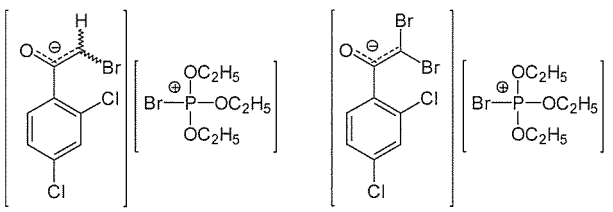

Fig. 4. Ion pairs suspected of playing a key role in the formation of **1** and **2**.

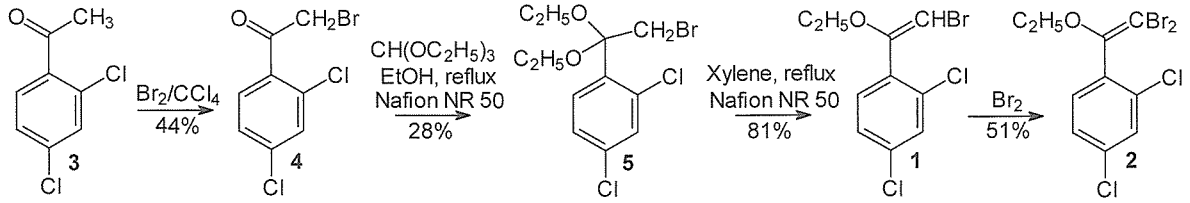

Fig. 5. Synthesis of **1** and **2**.

dichloro)styrene (**1**) and 2,2-dibromo-1-ethoxy-(2′,4′-dichloro)styrene (**2**) surprisingly failed.[20]

In our hands the independent synthesis of **1** and **2** succeeded. Comparative analysis of the synthesized compounds with the identified **1** and **2** matched their structures with the proposed structures of the investigated impurities.

1 and **2** were obtained from 2,4-dichloroacetophenone (**3**), as shown in Fig. 5.

2,4-Dichloroacetophenone (**3**) was brominated to 2,4-dichlorophenacyl bromide (**4**), which was obtained in 44% yield as a certified reference material of 99.8% purity (greater than the purity of **4** commercially available). Compound **4** was acetalized with ethyl orthoformate in the presence of various acidic catalysts in anhydrous ethanol. Using 4-toluenesulfonic acid led to 2,4-dichlorophenacyl bromide diethyl ketal (**5**) in only 7–9% yield. Other acidic catalysts, such as concentrated sulfuric acid, silica gel, alumina, and montmorilonit K, failed. Compound **5** was obtained in 28% yield when superacidic fluorinated resin (Nafion NR 50)[24–26] was used. Ethanol was eliminated from **5** in boiling xylene in the presence of an acidic catalyst. Using 4-toluenesulfonic acid led to **1** in 55% yield (sum of isomers). The yield of **1** was increased to 82% (a sum of isomers) when Nafion NR 50 was used as a catalyst. Bromination of **1** afforded **2** in 51% yield. Both synthesized **1** and **2** were characterized by spectral methods (GC MS, ^{1}H and ^{13}C NMR, IR). The retention times and El MS of synthesized **1** and **2** were fully consistant with the respective data of **1** and **2** observed during the bromfenvinphos analysis.

As **1** and **2** are impurities of bromfenvinphos, their insecticidal activity against house fly (*Musca domestica*), oriental cockroach (*Blatta orientalis*), granary weevil (*Sitophilus granarius*), and two-spotted red spider mite (*Tetranychus urticae*) was tested. Bromfenvinphos was used as a reference compound. No insecticidal activity of **1** and **2** was revealed.

Conclusion

2-Bromo-1-ethoxy-(2′,4′-dichloro)styrene (**1**) (as a mixture of geometric isomers) and 2,2-dibromo-1-ethoxy-2′,4′-dichloro)-styrene (**2**) were recognized as bromfenvinphos impurities. They were independently synthesized and fully characterized.

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的で，OTFP処理を解除することによって，EGA反応の強度および再分極時間はともに回復した．非フッ素化類縁体3-オクチルチオプロパン-2-オン（3-octhylthiopropan-2-one, OTP）は，フェロモンに対するEGA反応の強度にも2/3 RTにも影響が無く，この種の化合物におけるフッ素原子の重要性を示唆した．本研究の結果は，将来に向けてFAW制御におけるOTFPの応用に結び付くであろう．

（文責：編集事務局）

インド各地におけるネッタイイエカ *Culex quinquefasciatus* の殺虫剤抵抗性

Dev: Shankar Suman, Sachin N. Tikar, Brahma Dutta Parashar, Shri Prakash

ネッタイイエカ *Culex quinquefasciatus* は，リンパフィラリア症の主要媒介体として知られている．ここでは，インドにおけるネッタイイエカ *Culex pipiens quinquefasciatus* Say, 1823の4種，Jodhpur（JD），Bikaner（BKN），Jamnagar（JMN）およびBathinda（BTH）を用いて，実験室で飼育している感受性種と比較しながら，テメホス，フェンチオン，*Bacillus thuringiensis israilensis* とNeemarin（主成分アザディラクチン）などの殺幼虫剤，およびシペルメトリン（cypermethrin），アルファシペルメトリン（alpha cypermethrin）とラムダシハロトリン（lambda cyhalothrin）などの殺成虫剤に対する抵抗性について報告する．野外種と実験室種の間のLC_{50}について抵抗性比（RR）を表した．JD種は，テメホス，フェンチオン，Neemarinおよびシペルメトリンに対して，それぞれ10.8，6.94，5.29と2.82倍の抵抗性を示した．BTH種は，テメホス，フェンチオン，ラムダシハロトリン，アルファシペルメトリンとシペルメトリンに対して抵抗性を示した（それぞれ9.06，2.06，3.33，4.96と3.19倍）．BKN種において，テメホス，フェンチオン，NeemarinおよびアルファシペルメトリンのRRはそれぞれ5.17，4.12，4.33と3.04倍であった．しかし，JMN種においては，アルファシペルメトリンとフェンチオンを除いたほとんどの殺虫剤においてRRは低かった．本研究の結果は，フェンチオンとテメホス抵抗性種の *C. quinquefasciatus* に対して，幼虫の制御に *B. thuringiensis israilensis* とNeemarinは効果的で，成虫の制御にはラムダシハロトリンとシペルメトリンの有効であることを示した．

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1-置換フェニル-3-(5-ハロベンゾイミダゾール-2-イル）アシル尿素の合成と抗真菌活性

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5-ハロベンゾイミダゾール-2-イルアシルイソシアネートと置換アニリンとの反応により，62.4%~76.1%の収率で，12種の新規な1-置換フェニル-3-(5-ハロベンゾイミダゾール-2-イル）アシル尿素を合成し，それらの構造解析を，IR，^{1}H NMRスペクトルおよび元素分析で行った．菌糸生育試験により，*Botrytis cinerea* と *Sclerotinia sclerotiorum*（*S. s*）に対する抗真菌活性を評価したところ，表題のほとんどの化合物は *S. s* に対して優れた抗真菌活性を示し，チオファネートメチルの活性を上回った．

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2-ブロモ-および2,2-ジブロモ-1-エトキシ-(2′,4′-ジクロロ）スチレン：工場製造されたブロムフェンビンホスに存在する2種の不純物の同定・合成および構造の完全解析

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殺虫剤ブロムフェンビンホスは，工業的に94~96%の純度で製造されるが，主成分のブロムフェンビンホスの他に10種類以上の不純物の存在が確認されている．その中の，2種の不純物が，2-ブロモ-1-エトキシ-(2′,4′-ジクロロ）スチレン（幾何異性体混合物）および2,2-ジブロモ-1-エトキシ-(2′,4′-ジクロロ）スチレンであることを，MS解析により新たに同定した．そして，この2種の不純物を，2′,4′-ジクロロアセトフェノンから別途に合成し，分光学的に解析したところ，工業製造されたブロムフェンビンホス中の不純物として以前に同定されていた化合物と同一であることが判明した．

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