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Insect Growth Regulators. Analogues of TH-6038 and TH-6040

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A number of analogues of the insect growth regulators TH-6038 (**1**) and TH-6040 (**2**) were synthesized and tested against four species of insects. The effects of selective replacement of oxygen by sulfur in **1** and **2**, as well as of various other structural modifications of these compounds, were determined. Although none of the new compounds were as active as **2**, several effectively inhibited larval development of all insects tested, and one compound, *N*-(4-chlorophenyl)-*N'*-(2,6-difluorobenzoyl)thiourea, inhibited reproduction of female house flies when administered in their diet at a concentration of 1%.

Chemicals capable of selectively disrupting the development of immature insects have become of ever increasing interest over the past several years. Two such compounds, 1-(4-chlorophenyl)-3-(2,6-dichlorobenzoyl)urea (TH-6038, Thompson-Hayward 6038, **1**) and 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea (TH-6040, Thompson-Hayward 6040, Dimilin, **2**) are noteworthy for several reasons. (1) They are effective against a broad spectrum of insect larvae (Wellinga et al., 1973a,b). (2) They are not only chemically dissimilar to the previously developed insect growth regulators, i.e. juvenile hormone mimics, but they are also biologically dissimilar in that they are lethal to a variety of insects at all larval stages. Thus they are effective against the feeding stages of some crop pests whereas juvenile hormone mimics may control the pests only after considerable feeding damage has been done. (3) They have the ability to effectively sterilize adult females of several insect species (Moore and Taft, 1975; Taft and Hopkins, 1975; also unpublished results from our laboratories).

The antifertility property of **1** and **2** has been of limited utility, however, because of the ability of the insects to rather rapidly regain fertility after exposure to the chemicals is terminated (Robbins et al., 1976; McHaffey, 1976). During the development of compounds **1** and **2**, the Philips–Duphar group thoroughly examined the effects of different substituents on the aromatic rings and also of substitution of nitrogen (Wellinga et al., 1973a,b), but they did not report chemosterilant activity of these compounds. We became interested in whether minor modifications in the structures of **1** and **2** might moderate the biological activities in this or any other respect and, accordingly, synthesized analogues wherein the oxygen atoms of **1** and **2** were individually replaced by sulfur atoms (**3**–**6**). We also prepared the trifluoro analogue **7**, the sulfonylurea **8** (replacement of C=O of **2** by SO_2), the carbamate **9** (replacement of NH of **1** by O), the benzoxazole derivative **11** (construction of an *O*-aryl bond in **2**), and the related compounds **7**, **10**, and **12**.

After this work was complete, Yu and Kuhr (1976) reported the synthesis and activity against seedcorn maggot larvae (*Hylemya platura* (Meigen)) of several 1-phenyl-3-benzoylureas and thioureas, including three compounds reported in this paper (**5**, **6**, and **7**). Our melting points are in good agreement with those reported.

MATERIALS AND METHODS

Syntheses of new compounds are outlined in Scheme I and are described in the Experimental Section; most were based on analogies in the literature. Worthy of note are the one-step synthesis of 2,6-difluorobenzenesulfonyl chloride **20**, and the different behaviors of the two benzoyl isothiocyanates, **15** and **16**, with 4-chlorophenol and aluminum chloride. The benzoxazole **11** was prepared by two independent methods to ensure a correct structural assignment.

The larval test systems for the yellow fever mosquito, *Aedes aegypti* (L.), the confused flour beetle, *Tribolium confusum* Jacquelin duVal, the house fly, *Musca domestica*

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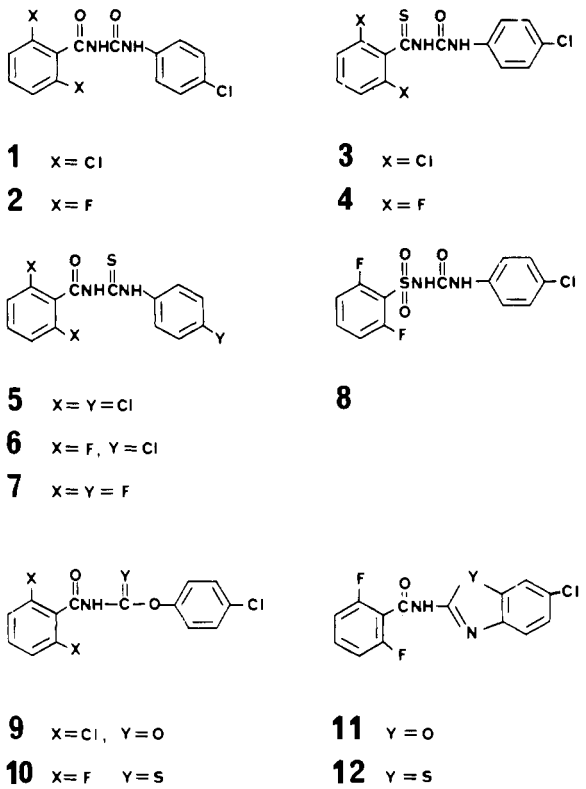
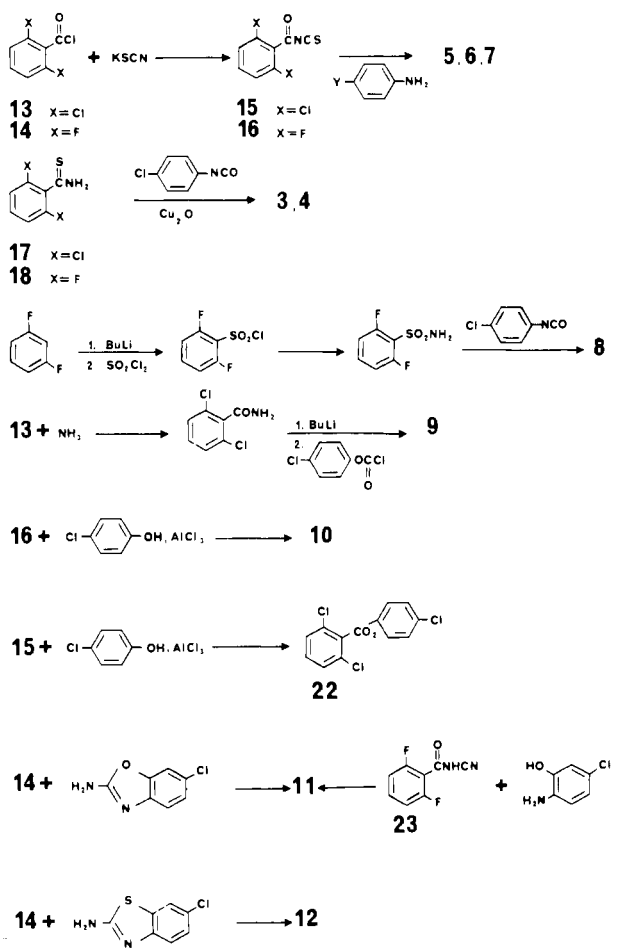


Scheme I



L., and the tobacco hornworm, *Manduca sexta* (L.), have been previously described (Robbins et al., 1975). The assays used to determine the effects of these compounds on reproduction of the house fly and the confused flour beetle were those previously used to assess the effects of ecdysones and synthetic analogues (Robbins et al., 1970) and all compounds were tested at a concentration of 1.0% in the adult diet.

EXPERIMENTAL SECTION

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

***N*-(4-Chlorophenyl)-*N'*-(2,6-difluorobenzoyl)thiourea (6), *N*-(4-Fluorophenyl)-*N'*-(2,6-difluorobenzoyl)thiourea (7), and *N*-(4-Chlorophenyl)-*N'*-(2,6-dichlorobenzoyl)thiourea (5).** A mixture of 2,6-difluorobenzoyl chloride (14) (Bunton and Roe, 1968) (9.0 g, 0.051 mol) and potassium thiocyanate (6 g, 0.06 mol) in acetonitrile (90 ml) was refluxed 45 min and then was cooled and filtered through Celite. The filtrate, containing 2,6-difluorobenzoyl isothiocyanate (16), was divided into two equal portions; the first was treated dropwise with a solution of *p*-chloroaniline (4.0 g, 0.027 mol) in acetonitrile. A mildly exothermic reaction occurred, the mixture was chilled, and 6 was collected by filtration (6.82 g, 84%, mp 190–191.5 °C). Recrystallization (2-propanol + 2-butanone) did not change the melting point. Anal. Calcd for $C_{14}H_9ClF_2N_2OS$: C, 51.45; H, 2.78; N, 8.58. Found: C, 51.49; H, 2.75; N, 8.55.

Similar treatment of the second portion of the solution of 16 with *p*-fluoroaniline (3 g) provided 6.03 g (81%) of 7 in two crops, mp 183–184.5 °C. Anal. Calcd for $C_{14}H_9F_3N_2OS$: C, 54.19; H, 2.92; N, 9.03. Found: C, 54.30; H, 2.85; N, 8.94.

Compound 5 was prepared analogously from 2,6-dichlorobenzoyl chloride (13) (Kohll and Fekkes, 1968), potassium thiocyanate, and *p*-chloroaniline (63%, mp 228.5–230.5 °C). Anal. Calcd for $C_{14}H_9Cl_3N_2OS$: C, 46.75; H, 2.52; N, 7.79. Found: C, 46.88; H, 2.45; N, 7.73.

2,6-Dichlorothiobenzamide (17). Hydrogen sulfide was bubbled through a warm solution of 2,6-dichlorobenzonitrile (16.4 g), pyridine (100 ml), and diethylamine (15 ml). Another 15 ml of diethylamine in 10 ml of pyridine was added in portions over 2.5 h, after which time the flow of H_2S was discontinued. The solvent was stripped, and the residue was partitioned between chloroform and aqueous hydrochloric acid. The chloroform solution was washed with water and with aqueous sodium bicarbonate and then was dried and evaporated to give 15 g of 17, mp 147–149 °C (Shell Research Ltd., 1962; lit. mp 151–152 °C).

***N*-(4-Chlorophenyl)-*N'*-[(2,6-dichlorophenyl)carbonothioyl]urea (3).** A mixture of 2,6-dichlorothiobenzamide (17) (4.57 g, 0.022 mol), *p*-chlorophenyl isocyanate (3.41 g, 0.022 mol), and cuprous oxide (0.5 g) in xylene (70 ml) (Cohen, 1974) was slowly heated to reflux and then held at that temperature for 7 min. The hot solution was filtered, and the filtrate upon cooling deposited 3 (3.95 g, 50%, mp 207 °C). Recrystallization from 2-propanol did not change the melting point. Anal. Calcd for $C_{14}H_9Cl_3N_2OS$: C, 46.75; H, 2.52; N, 7.79. Found: C, 46.94; H, 2.66; N, 8.00.

***N*-(4-Chlorophenyl)-*N'*-[(2,6-difluorophenyl)carbonothioyl]urea (4).** 2,6-Difluorobenzonitrile was converted to 2,6-difluorothiobenzamide (18) as described for the conversion of 2,6-dichlorobenzonitrile to 17. This conversion was difficult to reproduce, and the product was difficult to purify; accordingly, crude 18 (mp 115–118 °C) was not characterized but was reacted directly with *p*-chlorophenyl isocyanate as described for the conversion of 17 to 3. The 4 thus obtained had mp 195–196 °C after

Table I. Range of Concentrations of Test Compounds in Larval Diet or Medium Required to Inhibit Development or Kill 75% of the Test Insects

Compd	Tobacco hornworm, ppm	Yellow fever mosquito, ppm		Confused flour beetle larval test, ppm	House fly larval test, ppm
		First-instar	Fourth-instar		
2	0.1-0.5	0.001-0.01	0.001-0.01	0.5-1.0	0.015-0.075
3	1-5[a]	0.01-0.1	1.0-10.0	>1000[a]	>150[a]
4	0.1-0.5	0.01-0.1	0.01-0.1	500-1000	15-150
5	0.1-0.5	0.01-0.1	0.1-1.0	>1000	1.5-15
6	0.1-0.5	0.001-0.01	0.01-0.1	1-5	0.15-1.5
7	0.1-0.5	0.01-0.1	0.1-1.0	>1000	>150
8	1-5	1.0-10.0	>10[a]	>1000	>150
9	>5	>1[a]	>10	>1000	>150
10	>5	>1	>10	>1000	>150
11	>5	>1	>10	>1000	>150
12	<5	0.1-1	0.1-1.0	>1000	15-150
22	<5	>1	>10	>1000	>150

[a] Maximum test concentration.

recrystallization from 2-propanol plus a little 2-butanone. Anal. Calcd for $C_{14}H_9ClF_2N_2OS$: C, 51.45; H, 2.78; N, 8.58. Found: C, 51.69; H, 2.74; N, 8.60.

2,6-Difluorobenzenesulfonyl Chloride (20). 2,6-Difluorophenyllithium (0.1 mol) was prepared at −78 °C as described (Bunton and Roe, 1967) and the cold slurry was added dropwise, by means of a dry ice cooled addition funnel, to a solution of sulfuryl chloride (0.1 mol) in toluene (70 ml) which was also cooled to ca. −60 °C. The resulting mixture was allowed to warm to room temperature and then was poured into cold, saturated ammonium chloride. The layers were separated and the aqueous phase was extracted with toluene. The combined organic portions were washed with water and with brine and then were dried and concentrated. Distillation of the residue gave 6.8 g (32%) of **20**, bp 127.5–129.5 °C (6.5 mm).

2,6-Difluorobenzenesulfonamide (21). A solution of **20** (5.1 g) in acetone (5 ml) was added dropwise to 10 ml of cold 29% ammonium hydroxide. The mixture was acidified with dilute hydrochloric acid and **21** was collected by filtration (4.0 g, 60%, mp 180–184 °C). The analytical sample had mp 191–193 °C (2-propanol). Anal. Calcd for $C_6H_5F_2NO_2S$: C, 37.30; H, 2.61; N, 7.25. Found: C, 37.43; H, 2.54; N, 7.14.

***N*-(4-Chlorophenyl)-*N'*-[(2,6-difluorophenyl)-sulfonyl]urea (8).** A solution of potassium hydroxide (0.98 g) in methanol (7 ml) was added dropwise to a cold, stirred solution of **21** (2.90 g) in acetone (20 ml). The resulting solution was similarly treated with a solution of 4-chlorophenyl isocyanate (2.4 g) in acetone (20 ml). A white solid soon separated from solution. After 0.5 h at 0 °C the solid was collected, washed with a little cold acetone, suspended in water, and neutralized with acetic acid (4 ml). The mixture was stirred a few minutes; then the solid was collected (4.23 g, 81%, mp 153–156 °C). Recrystallization from acetic acid–water gave pure **8**, mp 165–166 °C. Anal. Calcd for $C_{13}H_9ClF_2N_2O_3S$: C, 45.03; H, 2.62; N, 8.08. Found: C, 45.28; H, 2.50; N, 8.01.

4-Chlorophenyl (2,6-Dichlorobenzoyl)carbamate (9). A cold (−60 °C) suspension of 2,6-dichlorobenzamide (7.6 g, 0.04 mol) in tetrahydrofuran (70 ml) was treated dropwise with *n*-butyllithium (0.04 mol of 1.6 M solution in hexane). After 10 min at −60 °C a solution of 4-chlorophenyl chloroformate (3.8 g, 0.02 mol) in tetrahydrofuran (15 ml) was added dropwise. After 5 more min, additional portions of butyllithium (0.02 mol) and the chloroformate (0.01 mol) were added in the same order as before. The process was repeated a third time (0.01 mol of butyllithium and 0.005 mol of the chloroformate); then the mixture was allowed to warm to room temperature, and was neutralized with a little acetic acid. Ether was added and the solution was washed with water and with brine and then was dried ($MgSO_4$) and concentrated. Trituration of the residual oil with hexane–ethyl acetate affected the crystallization of a little unreacted 2,6-dichlorobenzamide. Filtration and concentration of the filtrate gave an oil that was triturated with boiling hexane to give 5.6 g of crude **9**. Recrystallization from ethanol–water (3:2) gave 3.95 g (27%) of **9**, mp 149–153 °C. Anal. Calcd for $C_{14}H_8Cl_3NO_3$: C, 48.80; H, 2.34; N, 4.07. Found: C, 48.60; H, 2.32; N, 4.20.

***O*-4-Chlorophenyl (2,6-Difluorobenzoyl)carbamothioate (10).** A cooled suspension of aluminum chloride (4.40 g, 0.033 mol) in methylene chloride (30 ml) was treated dropwise with a solution of 4-chlorophenol (3.21 g, 0.025 mol) in methylene chloride (15 ml) (based on Trivadi, 1961). The resulting mixture was stirred 15 min at room temperature and then was treated dropwise with a solution of 2,6-difluorobenzoyl isothiocyanate (**16**) (0.023 mol), prepared as in the synthesis of **6** except the acetonitrile was stripped and replaced with methylene chloride (15 ml). After 4 h at room temperature additional methylene chloride was added, followed by cold water. The layers were separated, and the organic phase was treated with 5% aqueous sodium hydroxide to precipitate the sodium salt of **10** which was collected by filtration (2.12 g). The salt was suspended in water and neutralized with acetic acid, and **10** was extracted into chloroform. The chloroform was dried and stripped, and the residue was triturated with hexane to give 1.20 g (16%) of **10** as a yellow solid, mp 107.5–109 °C. Recrystallization from heptane provided an analytical sample, mp 110–111.5 °C. Anal. Calcd for $C_{14}H_8ClF_2NO_2S$: C, 51.31; H, 2.46; N, 4.27. Found: C, 51.08; H, 2.47; N, 4.50.

4-Chlorophenyl 2,6-Dichlorobenzoate (22). When the preceding procedure was repeated with **15** in place of **16**, the desired carbamate was not obtained. Instead, the ester **22** (mp 94–96.5 °C) was isolated in 46% yield. The structure of **22** was confirmed by its elemental analysis, infrared spectrum (1760 cm^{-1}, ester C=O), and saponification to 4-chlorophenol and 2,6-dichlorobenzoic acid. Anal. Calcd for $C_{14}H_7Cl_3O_2$: C, 51.77; H, 2.34; Cl, 35.27. Found: C, 51.77; H, 2.20; Cl, 35.10.

***N*-(6-Chloro-2-benzoxazolyl)-2,6-difluorobenzamide (11). (a) From 6-Chloro-2-benzoxazolamine and 2,-6-Difluorobenzoyl Chloride.** A solution of 6-chloro-2-benzoxazolamine (Sam and Plampin, 1964) (1.68 g, 0.01 mol) and 2,6-difluorobenzoyl chloride (1.76 g, 0.01 mol) in chlorobenzene (20 ml) was refluxed 2 h. The hot solution was filtered; upon cooling **11** separated from solution and was collected by filtration. Recrystallization from chlorobenzene gave **11**, mp 208–210 °C (ca. 1.2 g, 39%).

Another recrystallization from acetonitrile did not affect the melting point. Anal. Calcd for $C_{14}H_7ClF_2N_2O_2$: C, 54.47; H, 2.29; N, 9.08. Found: C, 54.40; H, 2.49; N, 9.05.

(b) From 2-Amino-5-chlorophenol and *N*-Cyano-2,6-difluorobenzamide. A stirred solution of sodium cyanamide (4.81 g, 0.075 mol) in water (40 ml) was treated dropwise at room temperature with 4.41 g (0.025 mol) of **14**. After 1.5 h the mixture was chilled, and concentrated hydrochloric acid (6.5 ml) was added dropwise. *N*-Cyano-2,6-difluorobenzamide (**23**) separated from solution and was collected and dried (4.25 g, mp 137–137.5 °C, 93%). Anal. Calcd for $C_8H_4F_2N_2O$: C, 52.75; H, 2.21; N, 15.38. Found: C, 52.54; H, 2.03; N, 15.31.

A mixture of 2-amino-5-chlorophenol (0.88 g), **23** (1.12 g), and concentrated hydrochloric acid (0.5 ml) in absolute ethanol (8 ml) was refluxed 6 h and then was cooled and filtered. The filtrate was evaporated and the residue was triturated with ethyl acetate to give a light tan solid that was recrystallized from ethyl acetate–hexane to give **11**, mp 209–210 °C (0.13 g). The infrared spectrum of this material was identical with that of **11** prepared from **14** and 6-chloro-2-benzoxazolamine.

***N*-(6-Chloro-2-benzothiazolyl)-2,6-difluorobenzamide (12)** was prepared from **14** and 6-chloro-2-benzothiazolamine (Bhargava and Singh, 1961) by method a described for the synthesis of **11** (76%, mp 224–225 °C). Anal. Calcd for $C_{14}H_7ClF_2N_2OS$: C, 51.78; H, 2.17; N, 8.63; S, 9.87. Found: C, 51.61; H, 2.26; N, 8.73; S, 9.67.

RESULTS AND DISCUSSION

Several of the new compounds were active larval growth inhibitors (Table I). Compounds **3–7**, which most closely resemble **1** and **2**, were the most effective. Within this group, **4** was more effective than **3**, and **6** was superior to **5** (the difluoro compounds were more active than their dichloro counterparts just as **2** is more active than **1**). Compound **5** appeared more active than **3**, and **6** more active than **4** (the benzoylthioureas were more effective than the thiobenzoylureas). The sulfonylurea **8** had some activity, but was significantly less active than **3–7**. Neither of the carbamates **9** or **10** showed activity; this was not unexpected since the aniline NH of **1** was known to be essential for activity (Wellinga et al., 1973a). Although ester **22** was not a planned compound, it showed slight activity in the tobacco hornworm.

The benzoxazole **11**, which corresponds to a hypothetical oxidative cyclization product of **2**, had little or no activity against either the house fly or the yellow fever mosquito; on the other hand, the corresponding benzothiazole **12** did display some activity against each of these insects. This comparison provides an interesting contrast to the previous results; in the other examples, variations from the basic structure of **1** and **2** resulted in less active compounds (replacement of either oxygen with sulfur, a carbonyl group with a sulfonyl group, or a nitrogen with an oxygen). In this pair, the more active compound was in fact the one containing sulfur instead of oxygen.

None of the new compounds showed enhanced activity in disrupting reproduction. Only **6** showed any chemosterilant activity, and that consisted of partial and reversible sterility in female house flies at a dietary concentration of 1%; **2** is effective (although reversible) in inhibiting house fly reproduction at 0.05% and *Tribolium* reproduction at 0.5%.

In summary, we have synthesized several rather effective insect growth disruptors. Compounds **4–7** had activities comparable to that of **2** on the tobacco hornworm. The most effective compound against other insects is **6**; it approaches, within an approximate factor of 10, the activity of TH-6040 (**2**), and is perhaps comparable in activity to TH-6038 (we have not studied **1** in detail). Compound **6** appears to be only about $^1/_{10}$ to $^1/_{20}$ as active as **2** in inhibiting reproduction in the two species of insects studied.

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