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·研究简报·

含酰腙结构的新型吡唑酰胺衍生物对小菜蛾的生物活性

岳 敏, 袁勤坤, 金林红*

(贵州大学 精细化工研究开发中心,绿色农药与农业生物工程国家重点实验室培育基地/教育部重点实验室,贵阳 550025)

摘 要:采用浸虫法、夹毒叶片法和叶碟法分别测定了13个含酰腙结构的新型吡唑酰胺衍生物对小菜蛾3龄幼虫的触杀、胃毒和拒食活性。结果表明:该类化合物对小菜蛾3龄幼虫具有较高的胃毒和拒食活性,其中苯环上含有氯原子、且酰腙一端的取代基含有杂原子且体积较小的化合物**H7**的胃毒和拒食活性最好,明显高于对照药剂毒死蜱。**H7** 72 h胃毒作用LC_{50}值为0.6 mg/L(毒死蜱的LC_{50}值为7.4 mg/L);有10个化合物的拒食活性高于毒死蜱,其中**H7** 48 h的拒食中浓度(AFC_{50})最低,为0.6 mg/L,明显低于毒死蜱(AFC_{50} =6.5 mg/L)。供试化合物对小菜蛾3龄幼虫均无触杀活性。

关键词:酰腙;吡唑酰胺;小菜蛾;触杀活性;胃毒活性;拒食活性

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Insecticidal activities of novel pyrazole amides containing hydrazone substructures against *Plutella xylostella*

YUE Min, YUAN Qinkun, JIN Linhong*

(*Research and Development Center for Fine Chemicals, State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering/Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Guiyang* 550025, *China*)

Abstract: Thirteen novel pyrazole amides containing hydrazine moiety were detected for their contact, stomach and anti-feeding activity in laboratory against the 3rd instar larvae of *Plutella xylostella*, by using insect-dipping method, leaf sandwich method and leaf disc method respectively. The results showed that these compounds possessed high stomach activity and anti-feeding activity against the larvae. Among these compounds, **H7**, which contains chlorine atoms in benzene ring and heteroatom in the acylhydrazone moiety, had the strongest contact and stomach activity which is much higher than that of control agent chlorpyrifos. The results indicated that the LC_{50} value of 72 h stomach toxicity of **H7** and chlorpyrifos against *P. xylostella* were 0.6 and 7.4 mg/L, respectively. Additionally, there were 10 compounds that showed higher anti-feeding activity than that of chlorpyrifos against *P. xylostella*, and the 48 h AFC_{50} (concentration causing 50% antifeedant rate) value of **H7** was 0.6 mg/L, while that of

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作者简介:岳敏,男,硕士研究生;* **通信作者**(Author for correspondence):金林红,男,硕士,教授,硕士生导师,主要从事农药创新研究,**E-mail**:linhong_j@126.com

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chlorpyrifos was 6.5 mg/L. All tested compounds showed no contact activity against *P. xylostella*.

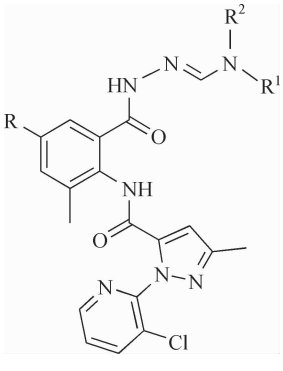
Key words: hydrazone; pyrazole amides; *Plutella xylostella*; contact activity; stomach activity; anti-feeding activity

吡唑酰胺类化合物具有很好的杀虫活性[1-3]，如拜耳公司和日本石原株式会社联合开发的氟虫酰胺[4]，杜邦公司开发的氯虫酰胺[5]和氰虫酰胺[6]等。这类杀虫剂均对鳞翅目害虫高效，且只作用于昆虫的鱼尼丁受体(RyRs)[7-8]，而对哺乳动物的鱼尼丁受体无效，是与其他杀虫剂无交互抗性且对环境友好的新型杀虫剂[9-10]。2010 年，本研究组以氯虫酰胺为先导结构，设计合成了一系列含酰腙结构的新型吡唑酰胺衍生物，初步生物活性测试结果表明，该类化合物具有较高的杀虫活性，且杀虫谱较广[11-13]。为了进一步确定该类化合物的杀虫作用方式，以及其对昆虫取食的影响，笔者以小菜蛾为试虫，研究了自行合成的 13 个含酰腙结构的吡唑酰胺衍生物对其幼虫的触杀、胃毒及拒食活性。

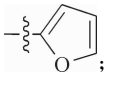
1 材料与方法

1.1 供试药剂

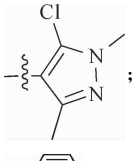
化合物 **H1 ~ H13** 均为本实验室合成并经结构表征[11]，结构式见 **Scheme 1**。以毒死蜱(chlorpyrifos)原药(纯度 95.7%，广西田园生化股份有限公司提供)为对照药剂。供试化合物及对照药剂均用 DMSO(二甲基亚砜)溶解，配制成有效成分为 4 000 mg/L 的贮存液，备用。



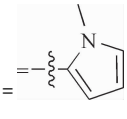
H1: R = Cl, R^1 = CH_3, R^2 = CH_3; **H2**: R = Cl, R^1 = H, R^2 = $CH_2CH_2CH_3$;
H3: R = Cl, R^1 = CH_3, R^2 = CH_2CH_3; **H4**: R = Cl, R^1 = CH_3, R^2 = $CH(CH_3)_2$;
H5: R = Cl, R^1 = H, R^2 = $CH(CH_3)_2$; **H6**: R = Cl, R^1 = H, R^2 = CH_2CH_3;
H7: R = Cl, R^1 = H, R^2 = $N(CH_3)_2$; **H8**: R = H, R^1 = H, R^2 = $CH_2CH_2CH_3$;



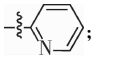
H9: R = Cl, R^1 = H, R^2 = ;



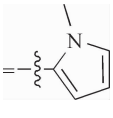
H10: R = Cl, R^1 = H, R^2 = ;



H11: R = Cl, R^2 = H, R^2 = ;



H12: R = Cl, R^1 = H, R^2 = ;



H13: R = H, R^1 = H, R^2 = ;

Scheme 1

1.2 供试昆虫

供试昆虫为贵州大学精细化工研究开发中心实验室用萝卜苗和甘蓝连续饲养 3 代以上的敏感品系小菜蛾(虫源由贵州省农业科学院植物保护研究所提供)，室内饲养条件：温度 20 ~ 22 ℃，湿度 40% ~ 50%，光照 17 h。

1.3 实验方法

1.3.1 触杀活性测定 采用浸虫法[14]。取适量的各供试化合物的贮存液，用含质量分数为 0.5% 的 Tween-20 水溶液按等比稀释法配制成 5 个质量浓度梯度的药液供试。以生长状况一致的小菜蛾 3 龄初期幼虫为试虫，以甘蓝叶片为食料。每个处理 10 头幼虫，3 次重复。以只含 DMSO 的 Tween-20 水溶液为空白对照。72 h 后调查结果，用 DPS 数据处理系统分析，计算 LC_{50} 值和 95% 置信限。

1.3.2 胃毒活性测定 采用夹毒叶片法[15]。药液的配制方法同 1.3.1 节，但各化合物的初始浓度和浓度梯度需根据预实验结果确定。用毛笔将供试药液均匀地刷于甘蓝叶正面，晾干后制成直径 3 cm 的圆叶片，上面盖一张同样大小的甘蓝圆叶片，之间用淀粉浆糊粘贴，制成夹毒叶片。每个培养皿中放入 2 张夹毒叶片，接入 10 头已饥饿 4 h 的小菜蛾 3 龄幼虫。每处理 3 次重复。以只含 DMSO 的 Tween-20 水溶液为对照。72 h 后调查结果，用 DPS 数据处理系统分析，计算 LC_{50} 值和 95% 置信限。

1.3.3 拒食活性测定 参照吴文君[16]的叶碟法进行。药液配制方法同 1.3.1 节，但各化合物的初始浓度和浓度梯度需根据预实验结果确定。将处理组与空白对照组叶片交叉放置在培养皿中，接入饥饿

4 h 的小菜蛾 3 龄初期幼虫 10 头。每处理 5 次重复。48 h 后统计结果(以坐标纸方格数计算取食面积)。由(1)式计算拒食率。用 DPS 数据处理系统分析,计算拒食中浓度(AFC_{50})和 95% 置信限。

$$\text{拒食率}/\% = \frac{\text{对照组取食面积} - \text{处理组取食面积}}{\text{对照组取食面积} + \text{处理组取食面积}} \times 100 \quad (1)$$

2　结果与讨论

2.1　触杀活性

实验结果表明,供试化合物触杀活性均很差,LC_{50}值最低为 126.6 mg/L,远不及对照药剂毒死蜱(LC_{50}值为 12.2 mg/L)。

2.2　胃毒活性

供试化合物均具有较强的胃毒活性(见表 1),其中 **H7** 的作用最强,LC_{50}值为 0.6 mg/L,除 **H8**、**H12** 和 **H13** 外,其余化合物均表现出比毒死蜱更高的胃毒活性。

2.3　拒食活性

供试化合物对小菜蛾均有较好的拒食活性(见表 2),其中有 10 个化合物表现出比毒死蜱更强的拒食活性,而其中又以 **H7** 的活性最强,AFC_{50}值为 0.6 mg/L,其次是 **H3**,AFC_{50}值为 0.7 mg/L。

表 1　化合物 H1 ~ H13 对小菜蛾 3 龄幼虫的胃毒活性

Table 1　Stomach activity of compounds **H1 – H13** against 3rd instar larvae of *P. xylostella*

化合物 Compound	毒力回归方程 Toxicity regression equation	相关系数 Relative coefficient, r	LC_{50}/(mg/L)	95% 置信限 95% confidence limits/(mg/L)
H1	$y = 1.380\,8x + 4.935\,4$	0.994 8	1.1	0.8 ~ 1.6
H2	$y = 1.314\,1x + 4.506\,8$	0.999 5	2.4	1.6 ~ 3.5
H3	$y = 1.748\,2x + 4.968\,1$	0.998 8	1.0	0.8 ~ 1.4
H4	$y = 1.988\,8x + 4.561\,9$	0.989 2	1.7	1.3 ~ 2.2
H5	$y = 3.195\,0x + 3.423\,2$	0.993 9	3.1	2.5 ~ 3.8
H6	$y = 1.735\,1x + 4.287\,5$	0.973 9	2.6	1.9 ~ 3.4
H7	$y = 1.622\,3x + 5.400\,2$	0.987 3	0.6	0.4 ~ 0.8
H8	$y = 2.512\,4x + 1.651\,7$	0.990 4	21.6	16.6 ~ 27.9
H9	$y = 2.757\,8x + 4.068\,6$	0.989 2	2.2	1.8 ~ 2.6
H10	$y = 1.803\,4x + 3.534\,6$	0.995 8	6.5	4.8 ~ 8.7
H11	$y = 2.176\,8x + 4.092\,7$	0.994 0	2.6	2.0 ~ 3.5
H12	$y = 1.897\,9x + 3.145\,6$	0.986 3	9.5	6.6 ~ 13.7
H13	$y = 2.584\,8x + 1.599\,7$	0.991 8	20.7	16.5 ~ 25.9
毒死蜱 chlorpyrifos	$y = 1.581\,0x + 3.625\,4$	0.975 9	7.4	5.1 ~ 10.7

表 2　化合物 H1 ~ H13 对小菜蛾 3 龄幼虫的拒食活性

Table 2　Anti-feeding activity of compounds **H1 – H13** against 3rd instar larvae of *P. xylostella*

化合物 Compound	毒力回归方程 Toxicity regression equation	相关性系数 Relative coefficient, r	AFC_{50}/(mg/L)	95% 置信限 95% confidence limits/(mg/L)
H1	$y = 1.578\,5x + 5.015\,0$	0.973 2	1.0	0.9 ~ 1.0
H2	$y = 1.536\,4x + 4.618\,7$	0.980 8	1.8	1.6 ~ 1.9
H3	$y = 1.378\,8x + 5.197\,9$	0.987 8	0.7	0.7 ~ 0.8
H4	$y = 1.686\,6x + 5.503\,3$	0.969 8	0.9	0.9 ~ 1.0
H5	$y = 3.704\,2x + 3.020\,5$	0.978 9	3.4	3.3 ~ 3.5
H6	$y = 2.629\,3x + 4.546\,6$	0.964 9	1.5	1.4 ~ 1.6
H7	$y = 1.832\,7x + 5.386\,2$	0.991 9	0.6	0.6 ~ 0.6
H8	$y = 2.639\,4x + 1.229\,3$	0.979 3	26.8	25.8 ~ 27.9
H9	$y = 3.838\,7x + 3.878\,5$	0.973 2	2.0	1.9 ~ 2.0
H10	$y = 1.712\,5x + 4.105\,6$	0.975 8	3.3	3.1 ~ 3.5
H11	$y = 2.501\,9x + 3.919\,3$	0.981 7	2.7	2.6 ~ 2.8
H12	$y = 1.737\,2x + 3.240\,5$	0.986 9	10.2	9.6 ~ 10.9
H13	$y = 2.793\,8x + 1.306\,4$	0.975 0	21.0	20.2 ~ 21.8
毒死蜱 chlorpyrifos	$y = 3.537\,5x + 1.801\,7$	0.975 9	6.5	6.1 ~ 6.9

4 小结

研究结果表明:化合物 **H7** 的杀虫活性最好,其胃毒和拒食活性均明显优于对照药剂毒死蜱;供试化合物的触杀活性均较差,远低于毒死蜱,这可能与该类化合物脂溶性差,不易穿透幼虫表皮有关,有待进一步研究证实。

从化合物结构与活性的关系来看,苯环上是否含有氯原子、以及酰腙一端 R^2 取代基的大小对化合物的生物活性有较大影响:化合物 **H7** 在苯环上有氯原子取代,且 R^2 较小,具有很高的杀虫活性;而化合物 **H8** 和 **H13** 的苯环上均无氯原子,其活性很低;**H10** 和 **H12** 中虽含有氯原子,但 R^2 分别为体积较大的 1,3-二甲基-5-氯吡唑基和吡啶基,其活性明显低于其他含氯化合物;另外,R^2 为含杂原子的非环烃时可能会大大增加其活性(如 **H7** 的活性明显高于 **H5**)。这些初步的研究结果可为该类化合物的进一步结构优化提供一定参考。

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