

·研究论文·

## 2-苄硫基烟酰胺类衍生物的合成及生物活性

朱宇春<sup>2</sup>, 袁莉萍<sup>\*1</sup>, 曹 瑾<sup>1</sup>, 沈晓霞<sup>1</sup>, 吕冬华<sup>1</sup>  
倪长春<sup>1</sup>, 沈 宙<sup>1</sup>, 陈 亮<sup>1</sup>, 张一宾<sup>1</sup>

(1. 上海市农药研究所, 上海 200032; 2. 华东理工大学 药学院, 上海 200237)

**摘 要:**以 2-苄硫基烟酸为原料, 设计并合成了 26 个 2-苄硫基烟酰胺类化合物, 其化学结构经核磁共振氢谱和元素分析确证。初步的生物活性测定结果表明, 该类化合物具有一定的杀虫及除草活性。其中 C-9、C-10、C-11 在 50 mg/L 时对淡色库蚊 *Culex pipiens pallens* 的致死率达到 100%; C-3、C-6、C-15 在 100 mg/L 对稗草 *Echinochloa crusgalli* Link、马唐 *Digitaria sanguinalis*、苋菜 *Ambrosia tricolor* Linn 的白化度大于 80%。

**关键词:**烟酰胺; 衍生物; 合成; 生物活性

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## Synthesis and Bioactivity of 2-Benzylsulfanyl Nicotinamide Derivatives

ZHU Yu-chun<sup>2</sup>, YUAN Liping<sup>\*1</sup>, CAO Jin<sup>1</sup>, SHEN Xiao-xia, LV Dong-hua  
NI Chang-chun<sup>1</sup>, SHEN Zhou<sup>1</sup>, CHEN Liang<sup>1</sup>, ZHANG Yi-bin<sup>1</sup>

(1. Shanghai Pesticide Research Institute, Shanghai 200032, China; 2. East China University  
of Science and Technology, Pharmaceutical Institute, Shanghai 200237, China)

**Abstract:** In search for novel pesticides with high effects, high selectivity and low toxicity, 26 compounds belong to 2-benzylsulfanyl nicotinamide derivatives were designed and synthesized starting from 2-benzylsulfanyl nicotinic acid. Their chemical structures were confirmed by <sup>1</sup>H NMR and elemental analysis. Preliminary bioassays showed that some compounds exhibited certain insecticidal and herbicidal activities. The mortality of *Culex pipiens pallens* from C-9, C-10 and C-11 at the concentration of 50 mg/L reached 100%. The albino rate of C-3, C-6, C-15 to *Echinochloa crusgalli*, *Digitaria sanguinalis*, *Ambrosia tricolor* and *Brassica alboglabra* at the concentration of 100 mg/L was above 80%.

**Key words** nicotinamide; derivative; synthesis; bioactivity

在近几年开发的新农药中, 有一半以上为杂环化合物, 特别是含氮的杂环化合物更引人注目<sup>[1]</sup>。烟酰胺系维生素 B 族类物质, 主要存在于动物体内, 是辅酶 I 和辅酶 II 的组成部分, 对其衍生物的合成是建立在药理性质研究基础上的, 对

这一类衍生物的研究亦成为当今新农药开发的热点<sup>[2]</sup>。如由 May & Baker Ltd 开发的烟酰胺类除草剂吡氟草胺 (diflufenican) 以及由德国巴斯夫公司开发的新型烟酰胺类杀菌剂啉酰菌胺 (boscalid) 等<sup>[3, 4]</sup>。

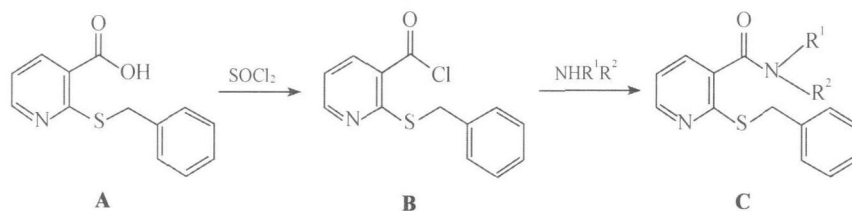
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作者简介: 朱宇春 (1983-), 女, 江苏人, 硕士研究生, E-mail: paopaoxiong8304@163.com; \*通讯作者 (Author for correspondence): 袁莉萍 (1964-), 女, 上海人, 教授级高级工程师, 主要从事新农药创制研究工作, 联系电话: 021-64644052; E-mail: spric@online.sh.cn

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为了进一步开发高效、高选择性、低毒且结构简单的活性化合物,笔者以 2-苄硫基烟酸为起始原料,设计合成了 26 个未见文献报道的 2-苄硫基烟酰胺类化合物,所有目标化合物结构经过核磁

共振氢谱和元素分析确证。初步生物活性测试表明部分化合物具有不同程度的杀虫、抑菌及除草活性。目标化合物合成路线如下:



## 1 合成实验

### 1.1 仪器与试剂

Bruker AC300 型核磁共振仪 (以  $\text{CDCl}_3$  为溶剂, TMS 为内标); WRS-1A 型数字熔点仪 (温度未校正)。所用试剂均为化学纯或分析纯。

### 1.2 中间体 B 的制备<sup>[5]</sup>

于 250 mL 的反应瓶中加入 2-苄硫基烟酸 (A) 2.45 g (0.01 mol)、二氯亚砷 30 mL 和 0.1 g DMF, 搅拌回流反应 8 h。将反应液冷却至室温减压蒸去过剩的二氯亚砷, 得到 2-苄硫基烟酰氯 (B)。

### 1.3 目标化合物 C 的合成<sup>[6]</sup>

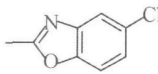

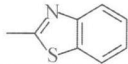
以化合物 2-苄硫基-N-苯基烟酰胺 (C-4) 的合

成为例。置苯胺 0.93 g (0.010 mol)、三乙胺 1.52 g (0.015 mol) 及二氯甲烷 30 mL 于 100 mL 反应瓶中, 冷却至 0℃, 滴加 2.64 g (0.01 mol) 化合物 B 溶于 15 mL 二氯甲烷的溶液, 室温反应 3 h。加入 50 mL 水, 分出有机相, 并经水洗、无水硫酸镁干燥, 减压脱溶得到深黄色粘稠液。经柱层析 [石油醚: 乙酸乙酯 (3:1, 体积比)] 分离提纯, 得到白色固体 2.35 g。收率 70.5%, 熔点: 167.1~168.4℃。

同法合成其他目标化合物, 其理化数据及元素分析数据见表 1,  $^1\text{H}$  NMR 数据见表 2。

表 1 化合物 C 的理化及元素分析数据

Table 1 Physical and elemental analytical data of compounds C

化合物 Compd.	$\text{R}^1$	$\text{R}^2$	熔点 m. p. / $^{\circ}\text{C}$	收率 Yield (%)	元素分析 (计算值, %)		
					Elemental analysis (Calcd., %)		
					C	H	N
C-1	H	2- $\text{CH}_3\text{C}_6\text{H}_4$	165.4~166.8	79.3	71.90 (71.83)	5.43 (5.42)	8.35 (8.38)
C-2	H	<i>n</i> - $\text{C}_4\text{H}_9\text{O}(\text{CH}_2)_3$	70.4~71.3	81.9	67.09 (67.01)	7.16 (7.31)	7.78 (7.81)
C-3	H	<i>n</i> - $\text{C}_3\text{H}_7$	123.2~123.7	90.4	67.10 (67.10)	6.28 (6.34)	9.81 (9.78)
C-4	H	$\text{C}_6\text{H}_5$	167.1~168.4	80.5	71.07 (71.22)	5.26 (5.03)	8.70 (8.74)
C-5	H	4- $\text{CF}_3\text{OC}_6\text{H}_4$	147.1~147.2	70.3	59.14 (59.40)	4.08 (3.74)	7.15 (6.93)
C-6	H	<i>i</i> - $\text{C}_3\text{H}_7$	125.4~125.8	91.3	67.12 (67.10)	6.30 (6.34)	9.68 (9.78)
C-7	H	4- $\text{ClC}_6\text{H}_4$	146.6~148.9	74.6	64.29 (64.31)	4.25 (4.26)	7.76 (7.89)
C-8	H		159.5~160.1	69.6	60.71 (60.68)	3.80 (3.56)	10.56 (10.61)
C-9	H		134.6~134.8	74.1	67.32 (67.27)	4.75 (4.70)	13.10 (13.07)
C-10	H	<i>cyclo</i> - $\text{C}_6\text{H}_{11}$	156.4~157.0	88.5	69.88 (69.90)	6.65 (6.79)	8.62 (8.58)
C-11	$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	117.3~117.6	50.4	67.91 (67.97)	6.65 (6.71)	9.30 (9.32)
C-12	H		165.5~167.1	65.4	63.65 (63.64)	3.97 (4.01)	11.15 (11.13)

续表 Continued

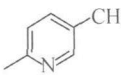
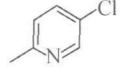
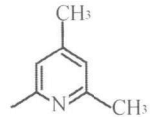
化合物 Compd.	R <sup>1</sup>	R <sup>2</sup>	熔点 m. p. /°C	收率 Yield( % )	元素分析(计算值, % ) Elemental analysis( Calcd. , % )		
					C	H	N
C-13	H		118.1 ~ 119.7	67.9	68.06 (68.04)	5.09 (5.11)	12.53 (12.53)
C-14	H		106.7 ~ 108.7	64.9	60.67 (60.76)	3.95 (3.97)	11.92 (11.81)
C-15	H	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	99.4 ~ 99.8	92.1	68.03 (67.97)	6.68 (6.71)	9.31 (9.32)
C-16	H	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	107.2 ~ 107.4	91.7	67.78 (67.97)	6.90 (6.71)	9.44 (9.32)
C-17	H	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	106.2 ~ 106.4	92.0	68.10 (67.97)	6.63 (6.71)	9.38 (9.32)
C-18	H	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	110.5 ~ 111.2	89.1	68.78 (68.75)	7.10 (7.05)	8.81 (8.91)
C-19	H	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> (CH <sub>3</sub> )CH	155.3 ~ 156.9	77.8	71.42 (71.32)	7.16 (7.01)	7.97 (7.88)
C-20	H	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	154.5 ~ 155.3	76.9	71.89 (71.83)	5.69 (5.42)	8.29 (8.38)
C-21	H		128.3 ~ 129.1	54.7	68.63 (68.74)	5.68 (5.48)	12.37 (12.02)
C-22	H	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	151.3 ~ 152.5	72.3	72.93 (72.91)	6.08 (6.12)	7.71 (7.73)
C-23	H	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	153.5 ~ 154.3	76.1	68.51 (68.55)	5.11 (5.18)	7.96 (7.99)
C-24	H	2-Cl,6-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	128.7 ~ 130.4	61.2	65.14 (65.12)	4.60 (4.65)	7.58 (7.69)
C-25	H	3-Cl,2-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	176.6 ~ 176.8	70.2	65.51 (65.12)	4.31 (4.65)	7.86 (7.69)
C-26	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	69.9 ~ 71.3	51.1	70.79 (70.75)	7.87 (7.92)	7.83 (7.86)

表 2 化合物 C 的核磁共振氢谱数据

Table 2 <sup>1</sup>H NMR data of compounds C

化合物 Compd	<sup>1</sup> H NMR (CDCl <sub>3</sub> /TMS),
C-1	2.32 (s, 3H, CH <sub>3</sub> ), 4.55 (s, 2H, SCH <sub>2</sub> ), 6.93 ~ 7.46 (m, 10H, A r H, A r H, PyH-5), 7.95 (s, 1H, NH), 8.01 (d, 1H, J = 5.70 Hz, PyH-4), 8.60 (d, 1H, J = 4.80 Hz, PyH-6)
C-2	0.88 (t, 3H, J = 7.35 Hz, CH <sub>3</sub> ), 1.25 ~ 1.35 (m, 2H, CH <sub>2</sub> ), 1.45 ~ 1.54 (m, 2H, CH <sub>2</sub> ), 1.83 ~ 1.91 (m, 2H, CH <sub>2</sub> ), 3.40 (t, 2H, J = 6.46 Hz, NCH <sub>2</sub> ), 3.53 ~ 3.59 (m, 4H, 2OCH <sub>2</sub> ), 4.47 (s, 2H, SCH <sub>2</sub> ), 6.90 (s, 1H, NH), 7.04 ~ 7.08 (m, 1H, PyH-5), 7.23 ~ 7.32 (m, 3H, A r H-3, 4, 5), 7.42 (d, 2H, J = 8.10 Hz, A r H-2, 6), 7.76 (d, 1H, J = 7.65 Hz, PyH-4), 8.52 (d, 1H, J = 4.80 Hz, PyH-6)
C-3	0.98 (t, 3H, J = 7.50 Hz, CH <sub>3</sub> ), 1.57 ~ 1.71 (m, 2H, CH <sub>2</sub> ), 3.36 ~ 3.43 (m, 2H, NCH <sub>2</sub> ), 4.49 (s, 2H, SCH <sub>2</sub> ), 6.34 (s, 1H, NH), 7.05 ~ 7.07 (m, 1H, PyH-5), 7.09 ~ 7.42 (m, 5H, A r H), 7.82 (d, 1H, J = 7.20 Hz, PyH-4), 8.52 (d, 1H, J = 4.65 Hz, PyH-6)
C-4	4.54 (s, 2H, SCH <sub>2</sub> ), 7.12 ~ 7.61 (m, 11H, A r H, A r H, PyH-5), 7.95 (d, 1H, J = 7.80 Hz, PyH-4), 8.06 (s, 1H, NH), 8.59 (d, 1H, J = 5.10 Hz, PyH-6)
C-5	4.54 (s, 2H, SCH <sub>2</sub> ), 7.13 ~ 7.33 (m, 6H, A r H-3, 4, 5, A r H-3, 5, PyH-5), 7.41 (d, 2H, J = 6.90 Hz, A r H-2, 6), 7.63 (d, 2H, J = 8.40 Hz, A r H-2, 6), 7.95 (d, 1H, J = 6.90 Hz, PyH-4), 8.16 (s, 1H, NH), 8.60 (d, 1H, J = 3.90 Hz, PyH-6)
C-6	1.25 (d, 6H, J = 6.00 Hz, 2CH <sub>3</sub> ), 4.22 ~ 4.29 (m, 1H, CH), 4.48 (s, 2H, SCH <sub>2</sub> ), 6.13 (s, 1H, NH), 7.04 ~ 7.09 (m, 1H, PyH-5), 7.21 ~ 7.33 (m, 3H, A r H-3, 4, 5), 7.41 (d, 2H, J = 8.10 Hz, A r H-2, 6), 7.80 (d, 1H, J = 7.50 Hz, PyH-4), 8.51 (d, 1H, J = 4.65 Hz, PyH-6)
C-7	4.12 (s, 2H, SCH <sub>2</sub> ), 7.04 ~ 7.11 (m, 1H, PyH-5), 7.22 ~ 7.32 (m, 5H, A r H-3, 4, 5, A r H-3, 5), 7.49 (d, 2H, J = 6.60 Hz, A r H-2, 6), 7.55 (d, 2H, J = 9.00 Hz, A r H-2, 6), 7.92 (d, 1H, J = 7.50 Hz, PyH-4), 8.22 (s, 1H, NH), 8.57 (d, 1H, J = 4.95 Hz, PyH-6)
C-8	4.43 (s, 2H, SCH <sub>2</sub> ), 6.88 ~ 6.92 (m, 1H, PyH-5), 7.07 (d, 1H, J = 8.42 Hz, A r H-6), 7.17 ~ 7.31 (m, 5H, A r H-3, 4, 5, 4, 7), 7.51 (d, 2H, J = 6.90 Hz, A r H-2, 6), 7.87 ~ 7.90 (m, 2H, PyH-4, NH), 8.46 (d, 1H, J = 3.60 Hz, PyH-6)

续表 Continued

化合物 Compd	$^1\text{H}$ NMR ( $\text{CDCl}_3/\text{TMS}$ ),
<b>C-9</b>	4. 46 (s, 2H, $\text{SCH}_2$ ), 6. 77 ~ 8. 63 (m, 12H, A $\text{H}$ , PyH, Py H), 11. 25 (s, 1H, NH)
<b>C-10</b>	1. 15 ~ 2. 04 (m, 10H, 5cyclo $\text{CH}_2$ ), 3. 93 ~ 4. 02 (m, 1H, CH), 4. 49 (s, 2H, $\text{SCH}_2$ ), 6. 19 (d, 1H, J = 6. 60 Hz, NH), 7. 05 ~ 7. 10 (m, 1H, PyH-5), 7. 21 ~ 7. 33 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 7. 20 Hz, A $\text{H}$ -2, 6), 7. 81 (d, 1H, J = 7. 65 Hz, PyH-4), 8. 51 (d, 1H, J = 4. 50 Hz, PyH-6)
<b>C-11</b>	1. 00 (t, 3H, J = 6. 90 Hz, $\text{CH}_3$ ), 1. 25 (t, 3H, J = 6. 90 Hz, $\text{CH}_3$ ), 3. 03 ~ 3. 10 (m, 2H, $\text{NCH}_2$ ), 3. 51 ~ 3. 58 (m, 2H, $\text{NCH}_2$ ), 4. 48 (s, 2H, $\text{SCH}_2$ ), 7. 04 ~ 7. 08 (m, 1H, PyH-5), 7. 22 ~ 7. 30 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 38 ~ 7. 43 (m, 3H, A $\text{H}$ -2, 6, PyH-4), 8. 51 (d, 1H, J = 4. 80 Hz, PyH-6)
<b>C-12</b>	4. 47 (s, 2H, $\text{SCH}_2$ ), 6. 87 ~ 7. 01 (m, 1H, PyH-5), 7. 19 ~ 7. 40 (m, 9H, A $\text{H}$ -2, 3, 4, 5, 6, 4, 5, 6, 7), 7. 83 (d, 1H, J = 7. 20 Hz, PyH-4), 7. 93 (s, 1H, NH), 8. 52 (d, 1H, J = 3. 60 Hz, PyH-6)
<b>C-13</b>	2. 26 (s, 3H, $\text{CH}_3$ ), 4. 48 (s, 2H, $\text{SCH}_2$ ), 7. 07 ~ 7. 11 (m, 1H, A $\text{H}$ , PyH-5), 7. 21 ~ 7. 27 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 6. 90 Hz, A $\text{H}$ -2, 6), 7. 56 (d, 1H, J = 8. 40 Hz, PyH-4), 7. 84 ~ 7. 87 (m, 2H, PyH-4, 6), 8. 25 (d, 1H, J = 8. 41 Hz, PyH-3), 8. 58 (d, 1H, J = 4. 80 Hz, PyH-6), 9. 03 (s, 1H, NH)
<b>C-14</b>	4. 49 (s, 2H, $\text{SCH}_2$ ), 7. 11 ~ 7. 14 (m, 1H, PyH-5), 7. 22 ~ 7. 31 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 6. 90 Hz, A $\text{H}$ -2, 6), 7. 70 (d, 1H, J = 8. 70 Hz, PyH-4), 7. 88 (d, 1H, J = 8. 10 Hz, PyH-4), 8. 10 (s, 1H, PyH-6), 8. 35 (d, 1H, J = 9. 00 Hz, PyH-3), 8. 60 (d, 1H, J = 4. 20 Hz, PyH-6), 8. 97 (s, 1H, NH)
<b>C-15</b>	0. 95 (t, 3H, J = 7. 20 Hz, $\text{CH}_3$ ), 1. 27 ~ 1. 42 (m, 2H, $\text{CH}_2$ ), 1. 54 ~ 1. 64 (m, 2H, $\text{CH}_2$ ), 3. 40 ~ 3. 47 (m, 2H, $\text{NCH}_2$ ), 4. 50 (s, 2H, $\text{SCH}_2$ ), 6. 27 (s, 1H, NH), 7. 07 ~ 7. 11 (m, 1H, PyH-5), 7. 22 ~ 7. 33 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 7. 50 Hz, A $\text{H}$ -2, 6), 7. 84 (d, 1H, J = 7. 20 Hz, PyH-4), 8. 53 (d, 1H, J = 4. 20 Hz, PyH-6)
<b>C-16</b>	0. 98 (d, 6H, J = 6. 60 Hz, 2 $\text{CH}_3$ ), 1. 85 ~ 1. 94 (m, 1H, CH), 3. 28 (t, 2H, J = 6. 30 Hz, $\text{NCH}_2$ ), 4. 50 (s, 2H, $\text{SCH}_2$ ), 6. 36 (s, 1H, NH), 7. 08 ~ 7. 12 (m, 1H, PyH-5), 7. 24 ~ 7. 33 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 6. 90 Hz, A $\text{H}$ -2, 6), 7. 84 (d, 1H, J = 8. 10 Hz, PyH-4), 8. 53 (d, 1H, J = 4. 50 Hz, PyH-6)
<b>C-17</b>	0. 97 (t, 3H, J = 7. 50 Hz, $\text{CH}_3$ ), 1. 22 (d, 3H, J = 6. 30 Hz, $\text{CH}_3$ ), 1. 52 ~ 1. 63 (m, 2H, $\text{CH}_2$ ), 4. 09 ~ 4. 14 (m, 1H, CH), 4. 50 (s, 2H, $\text{SCH}_2$ ), 6. 06 (d, 1H, J = 6. 00 Hz, NH), 7. 07 ~ 7. 11 (m, 1H, PyH-5), 7. 24 ~ 7. 33 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 6. 60 Hz, A $\text{H}$ -2, 6), 7. 82 (d, 1H, J = 7. 50 Hz, PyH-4), 8. 52 (d, 1H, J = 4. 80 Hz, PyH-6)
<b>C-18</b>	0. 99 (s, 9H, 3 $\text{CH}_3$ ), 3. 26 (d, 2H, J = 6. 30 Hz, $\text{NCH}_2$ ), 4. 52 (s, 2H, $\text{SCH}_2$ ), 6. 40 (s, 1H, NH), 7. 08 ~ 7. 13 (m, 1H, PyH-5), 7. 24 ~ 7. 33 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 41 (d, 2H, J = 6. 60 Hz, A $\text{H}$ -2, 6), 7. 88 (d, 1H, J = 7. 50 Hz, PyH-4), 8. 54 (d, 1H, J = 4. 80 Hz, PyH-6)
<b>C-19</b>	1. 00 ~ 1. 83 (m, 14H, 5cyclo $\text{CH}_2$ , CH, $\text{CH}_3$ ), 4. 03 ~ 4. 10 (m, 1H, CH), 4. 50 (s, 2H, $\text{SCH}_2$ ), 6. 18 (d, 1H, J = 8. 10 Hz, NH), 7. 06 ~ 7. 32 (m, 5H, A $\text{H}$ ), 7. 41 (d, 1H, J = 6. 60 Hz, PyH-5), 7. 83 (d, 1H, J = 7. 65 Hz, PyH-4), 8. 52 (d, 1H, J = 4. 50 Hz, PyH-6)
<b>C-20</b>	2. 34 (s, 3H, $\text{CH}_3$ ), 4. 54 (s, 2H, $\text{SCH}_2$ ), 7. 13 ~ 7. 49 (m, 10H, A $\text{H}$ , Ar H, PyH-5), 7. 95 (d, 1H, J = 7. 20 Hz, PyH-4), 8. 00 (s, 1H, NH), 8. 58 (d, 1H, J = 4. 65 Hz, PyH-6)
<b>C-21</b>	2. 35 (s, 3H, $\text{CH}_3$ ), 2. 39 (s, 3H, $\text{CH}_3$ ), 4. 50 (s, 2H, $\text{SCH}_2$ ), 6. 77 (s, 1H, PyH-5), 7. 08 ~ 7. 13 (m, 1H, PyH-5), 7. 23 ~ 7. 31 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 44 (d, 2H, J = 7. 20 Hz, A $\text{H}$ -2, 6), 7. 87 (d, 1H, J = 7. 50 Hz, PyH-4), 8. 01 (s, 1H, PyH-3), 8. 48 (d, 1H, NH), 8. 57 (d, 1H, J = 4. 80 Hz, PyH-6)
<b>C-22</b>	2. 32 (s, 9H, 3 $\text{CH}_3$ ), 4. 46 (s, 2H, $\text{SCH}_2$ ), 6. 93 (s, 2H, A $\text{H}$ -3, 5), 7. 09 ~ 7. 16 (m, 1H, PyH-5), 7. 22 ~ 7. 33 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 42 (d, 2H, J = 6. 90 Hz, A $\text{H}$ -2, 6), 7. 60 (s, 1H, NH), 8. 02 (d, 1H, J = 7. 80 Hz, PyH-4), 8. 59 (d, 1H, J = 3. 90 Hz, PyH-6)
<b>C-23</b>	3. 85 (s, 3H, $\text{CH}_3$ ), 4. 52 (s, 2H, $\text{SCH}_2$ ), 6. 90 (s, 1H, NH), 6. 99 ~ 7. 43 (m, 7H, A $\text{H}$ -3, 4, 5, 4, 5, 6, PyH-5), 7. 44 (d, 2H, J = 6. 60 Hz, A $\text{H}$ -2, 6), 7. 92 (d, 1H, J = 7. 20 Hz, PyH-4), 8. 51 (d, 1H, J = 7. 50 Hz, A $\text{H}$ -3), 8. 58 (d, 1H, J = 5. 10 Hz, PyH-6)
<b>C-24</b>	2. 38 (s, 3H, $\text{CH}_3$ ), 4. 55 (s, 2H, $\text{SCH}_2$ ), 7. 14 ~ 7. 33 (m, 7H, A $\text{H}$ -3, 4, 5, 3, 4, 5, PyH-5), 7. 44 (d, 2H, J = 7. 50 Hz, A $\text{H}$ -2, 6), 7. 79 (s, 1H, NH), 8. 04 (d, 1H, J = 7. 50 Hz, PyH-4), 8. 61 (d, 1H, J = 4. 80 Hz, PyH-6)
<b>C-25</b>	2. 36 (s, 3H, $\text{CH}_3$ ), 4. 56 (s, 2H, $\text{SCH}_2$ ), 7. 14 ~ 7. 34 (m, 7H, A $\text{H}$ -3, 4, 5, 3, 4, 5, PyH-5), 7. 42 (d, 2H, J = 7. 50 Hz, A $\text{H}$ -2, 6), 7. 79 (d, 1H, J = 8. 40 Hz, PyH-4), 8. 07 (s, 1H, NH), 8. 61 (d, 1H, J = 4. 65 Hz, PyH-6)
<b>C-26</b>	0. 73 (t, 3H, J = 7. 35 Hz, $\text{CH}_3$ ), 0. 96 (t, 3H, J = 7. 35 Hz, $\text{CH}_3$ ), 1. 02 ~ 1. 09 (m, 2H, $\text{CH}_2$ ), 1. 33 ~ 1. 45 (m, 4H, 2 $\text{CH}_2$ ), 1. 60 ~ 1. 68 (m, 2H, $\text{CH}_2$ ), 2. 96 (t, 2H, J = 7. 65 Hz, $\text{NCH}_2$ ), 3. 46 (t, 2H, J = 7. 65 Hz, $\text{NCH}_2$ ), 4. 48 (s, 2H, $\text{SCH}_2$ ), 7. 03 ~ 7. 07 (m, 1H, PyH-5), 7. 21 ~ 7. 30 (m, 3H, A $\text{H}$ -3, 4, 5), 7. 38 ~ 7. 42 (m, 3H, A $\text{H}$ -2, 6, PyH-4), 8. 48 (d, 1H, J = 3. 90 Hz, PyH-6)

## 2 生物活性

按《国家南方农药创制中心生测标准程序》,对所有化合物进行了杀虫、杀菌、除草的室内生物活性测试,由于所有化合物基本无杀菌活性,而在杀虫活性方面,仅对淡色库蚊表现出一定的活性。故本文仅介绍对淡色库蚊及除草活性的测试方法。称取一定量的药物,加入质量分数为 2%的 DMF 使其溶解,用无菌水稀释成 1 000 mg/L 母液。然后再用无菌水分别稀释成 500、250、125、100 mg/L 系列浓度药液备用。

### 2.1 杀虫及除草活性测定

采用 SOP 叶片浸渍法,测试化合物在 50 mg/L 浓度下对淡色库蚊 *Culex pipiens pallens* 的杀虫活性。试验重复 3 次,设空白对照。

采用平皿法,测定化合物在 100 mg/L 浓度下对稗草 *Echinochloa crusgalli* Link、马唐 *Digitaria sanguinalis*、苋菜 *Ambrosia tricolor* Linn 的除草活性。试验重复 3 次,设空白对照。

### 2.2 结果与讨论

由测定结果(表 3、表 4)可见,部分化合物具有明显的杀虫和除草(白化)活性。

表 3 50 mg/L 浓度下部分化合物对淡色库蚊的致死率

Table 3 The mortality to *Culex pipiens pallens* of some compounds at 50 mg/L

化合物 Compd	死亡率 Mortality (%)
C-9	100
C-10	100
C-11	100
C-18	88
C-24	83

从杀虫活性测试结果可以看出,化合物 C-9、C-10、C-11、C-18、C-24、C-26 对淡色库蚊表现出良好的致死活性,其中 C-9、C-10、C-11 在浓度为 50 mg/L 时致死率皆为 100%,而这些化合物结构中的 R<sup>1</sup>、R<sup>2</sup> 基团为吡啶基及烷基,因此可进一步对 2-苄硫基 N-吡啶基、N-环烷基烟酰胺结构的新化合物进行研究。

表 4 100 mg/L 下部分化合物的除草活性

Table 4 Herbicidal activity of some compounds at 100 mg/L

化合物 Compd	白化率 Albino rate (%)		
	苋菜 A. tricolor	稗草 E. crusgalli	马唐 D. sanguinalis
C-3	>80	>80	>80
C-6	>80	>80	>80
C-11	0	>80	0
C-15	>80	>80	>80
C-16	50	0	0
C-17	50	>80	>50

从除草活性测试结果可以看出, C-3、C-6、C-15 对稗草的白化度均大于 80%; C-3、C-6、C-11、C-15、C-17 对马唐的白化度均大于 80%; C-3、C-6、C-15 对苋菜的白化度均大于 80%。大致可以看出, C-3、C-6、C-15 对杂草具有一定的白化活性,说明此类化合物对杂草的光合作用可能具有一定的影响。从结构上看,这些化合物中的 N 取代基均为烷基,因此若以其为母体,进一步进行修饰和改造,极有可能开发出新型的除草剂。

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