

· 研究论文 ·

## 2-杂环基-1,3,4-噁二嗪酮类化合物的合成及其除草活性

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**摘要:**以取代杂环羧酸为起始原料,在1,3,4-噁二嗪-5-酮的2-位上分别引入咪唑环、吡啶环及氯代噻吩环,合成了31个未见报道的2-杂环基-1,3,4-噁二嗪酮化合物,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,该类化合物具有良好的除草活性,如在质量浓度200 mg/L时,化合物E14、E16、E20、E21对马唐 *Digitaria sanguinalis* 的抑制率大于90%,化合物E06、E07、E10、E14、E16、E20对苋菜 *Ambrosia tricolor* 的抑制率也大于90%。

**关键词:**1,3,4-噁二嗪-5-酮;有机合成;除草活性

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## Synthesis and herbicidal activity of 2-heterocyclic-1,3,4-oxadiazine-5-ones

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**Abstract:** Thirty one novel compounds of 2-heterocyclic-1,3,4-oxadiazine-5-one derivatives were synthesized through the starting material substituted heterocyclic carboxylic acid. The structure of all compounds was confirmed by <sup>1</sup>H NMR and elemental analysis. The preliminary assays showed that some compounds exhibited significant herbicidal activity. The inhibition rate of E14, E16, E20 and E21 to the *Digitaria sanguinalis* and E06, E07, E10, E14, E16 and E20 to the *Ambrosia tricolor* reached 90% at the mass concentration of 200 mg/L.

**Key words:** 1,3,4-oxadiazine-5-one; synthesis; herbicidal activity

杂环类农药的开发已成为当今世界新农药研发的热点之一,而其中'ó二嗪(oxadiazine)杂环化合物的研究开发亦引起了人们广泛的兴趣<sup>[1]</sup>,如茚虫威(indoxacarb)具有结构新颖,作用机制独特,用量

低,几乎对所有鳞翅目害虫有效,而对人类、环境、作物和非靶标生物安全等特点,是替代有机磷杀虫剂的理想品种之一<sup>[2]</sup>。笔者所在的研究小组对此类结构的化合物开展过一定研究,已发现2-取代苯基-

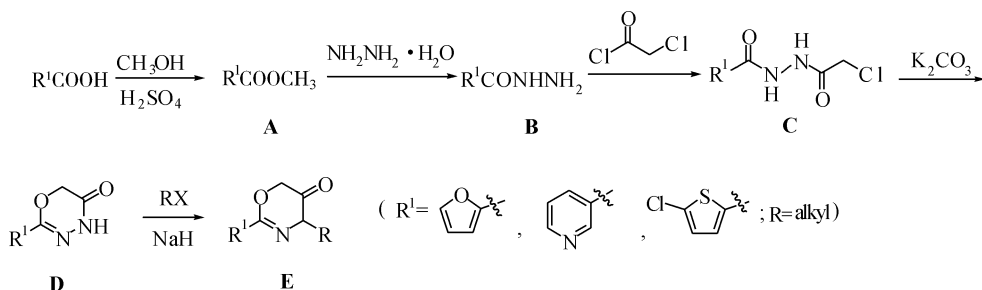
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1,3,4-*o* 二噻酮化合物<sup>[3]</sup>具有一定的杀菌活性,而2-取代苯乙炔基1,3,4-*o* 二噻酮化合物<sup>[4]</sup>具有一定的杀虫活性。在前期研究工作的基础上,将杂环基团(2-咪喃基、3-吡啶基、5-氯-2-噻吩基)引入至1,3,4-*o* 二噻酮环的2-位,并在4-位引入烷基。以杂环羧酸为原料,采用 **Scheme 1** 的合成路线,合成了一

系列未见文献报道的2-杂环基-1,3,4-*o* 二噻-5-酮的衍生物,并对其进行了杀虫、抗菌和除草的室内生物活性测定。结果发现此类化合物具有良好的除草活性,特别对马唐 *Digitaria sanguinalis* 和苋菜 *Ambrosia tricolor* Linn. 有较高的活性。



**Scheme 1**

## 1 实验部分

### 1.1 仪器与试剂

Bruker A 300 型核磁共振仪(以四甲基硅烷为内标,氘代氯仿为溶剂);Carloerba EA 元素分析仪;WRS 21A 型数字熔点仪(熔点未经校正);试剂为化学纯或分析纯。

### 1.2 化合物的合成

1.2.1 中间体 **A**、**B**、**C** 和 **D** 的制备 分别参照文献<sup>[5-8]</sup>的方法进行。

1.2.2 目标化合物 **E** 的制备 以化合物 **E01** 的合成例。参照文献<sup>[9]</sup>的方法进行。冰水浴冷却下,先将氢氧化钠 0.09 g(质量分数 60%, 2.25 mmol)加入到 100 mL 三口烧瓶中,再加入 *N,N*-二甲基甲酰胺(DMF) 10 mL 及 2-(2-咪喃基)-4-氢-1,3,4-*o* 二噻-5-酮(**D01**) 0.33 g(2.00 mmol),搅拌 15 min 后加入碘甲烷 0.45 g(3.17 mmol),反应液继续在 0 °C 下搅拌 4 h。向反应体系中加入二氯甲烷 50 mL 和水 100 mL,分出有机相并用水洗至中性,经无水硫酸钠干燥,脱溶得粗品。经硅胶柱层析(洗脱剂  $V_{\text{石油醚}}:V_{\text{乙酸乙酯}} = 4:1$ )分离提纯,得浅黄色固体 0.17 g,收率 47.2%。以不同卤代烃代替碘甲烷,用类似方法合成了其余 27 个目标化合物。

### 1.3 除草活性测定

按照《国家南方农药创制中心上海基地生测标准程序》——平皿法测定化合物在 200 mg/L 下对马唐 *Digitaria sanguinalis*、苋菜 *Ambrosia tricolor* Linn. 的除草活性。

1.3.1 药液的配制 将 100 mg 供试原药溶解于 5 mL *N,N*-二甲基甲酰胺(DMF)中,加入 0.25 mL 表面活性剂 OP-10,用水稀释至 100 mL,得质量浓度为 1 000 mg/L 的母液。试验时再用水依次稀释成不同浓度的供试药液。以不加原药者为空白对照。

1.3.2 测试方法 取马唐和苋菜种子各 5 粒置入垫有滤纸的平皿中,加入待测药液 10~15 mL,每处理设 3 个重复,并设空白对照;将处理好的种子置于光照培养箱内,在温度 28~30 °C、相对湿度 70%~80%、光照周期为 L/D = 16 h/8 h 的条件下培养。7 d 后调查结果。从株高、根长和生长相态 3 方面进行比较,根长度、相态与对照差异大的抑制率高,反之则低。



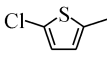



















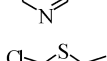
## 2 结果与讨论

### 2.1 化合物的合成

目标化合物的理化数据及元素分析数据见表 1,核磁(<sup>1</sup>H NMR)数据见表 2。对于目标化合物的合成,也有文献报道先将中间体 **A** 与取代脒反应,然后再与氯乙酰氯反应最终环合得到目标物<sup>[10]</sup>。但商品化的烷基取代脒品种很少,且不易得到,若采用该合成方法只能获得数量很少的目标物。本文报道的方法是先将中间体 **A** 与水合脒反应,接着再与氯乙酰氯反应,经环合得到中间体 **D**,**D** 再与各种卤代烃反应最终得到目标化合物。由于商品化的卤代烃品种很多,原料易得,故可得到数量众多的目标化合物,有利于进行构效关系分析。

表1 中间体 D 及目标化合物 E 的理化数据及元素分析数据

Table 1 Physical and elemental analytical data of compounds D and E

化合物 Compd.	R <sup>1</sup>	R	熔点 m. p. /°C or $n_D^{31}$	收率 Yield/%	元素分析(计算值)/%		
					Elemental analysis( Calcd. )/%		
					C	N	H
D01		H	148.3 ~ 150.0	16.90	50.55(50.61)	16.78(16.86)	3.68(3.64)
D02		H	196.4 ~ 197.2	32.50	54.11(54.24)	23.81(23.72)	3.92(3.98)
D03		H	190.4 ~ 192.0	31.50	38.73(38.81)	12.85(12.93)	2.37(2.33)
E01		CH <sub>3</sub>	114.4 ~ 115.4	47.20	53.29(53.33)	15.73(15.55)	4.59(4.48)
E02		C <sub>2</sub> H <sub>5</sub>	64.2 ~ 64.9	50.30	55.60(55.67)	14.45(14.43)	5.23(5.19)
E03		<i>n</i> -C <sub>3</sub> H <sub>7</sub>	45.2 ~ 45.4	52.40	57.62(57.69)	13.57(13.45)	5.73(5.81)
E04		<i>i</i> -C <sub>3</sub> H <sub>7</sub>	45.3 ~ 46.3	69.80	57.74(57.69)	13.48(13.45)	5.85(5.81)
E05		CH <sub>2</sub> CH = CH <sub>2</sub>	65.3 ~ 65.6	46.00	58.16(58.25)	13.66(13.59)	4.92(4.89)
E06		<i>n</i> -C <sub>4</sub> H <sub>9</sub>	41.8 ~ 42.5	56.80	59.52(59.45)	12.46(12.60)	6.32(6.37)
E07		<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	33.3 ~ 33.8	57.00	59.56(59.45)	12.71(12.60)	6.28(6.35)
E08		<i>i</i> -C <sub>4</sub> H <sub>9</sub>	84.1 ~ 84.5	41.80	59.43(59.45)	12.61(12.60)	6.38(6.35)
E09		CH <sub>2</sub> CH <sub>2</sub> CH = CH <sub>2</sub>	48.7 ~ 49.2	43.76	60.03(59.99)	12.60(12.72)	5.57(5.49)
E10		<i>i</i> -C <sub>5</sub> H <sub>11</sub>	46.5 ~ 47.0	56.00	61.13(61.00)	11.73(11.86)	6.88(6.83)
E11		CH <sub>3</sub>	145.4 ~ 146.9	46.90	56.50(56.54)	22.06(21.98)	4.66(4.74)
E12		C <sub>2</sub> H <sub>5</sub>	76.8 ~ 77.1	48.60	58.45(58.53)	20.34(20.48)	5.44(5.40)
E13		<i>n</i> -C <sub>3</sub> H <sub>7</sub>	68.5 ~ 69.0	51.60	60.31(60.26)	19.28(19.17)	5.89(5.98)
E14		<i>i</i> -C <sub>3</sub> H <sub>7</sub>	84.2 ~ 85.2	60.00	60.23(60.26)	19.11(19.17)	6.01(5.98)
E15		CH <sub>2</sub> CH = CH <sub>2</sub>	56.7 ~ 57.5	59.10	60.89(60.82)	19.32(19.34)	5.17(5.10)
E16		<i>n</i> -C <sub>4</sub> H <sub>9</sub>	56.5 ~ 57.4	59.00	61.71(61.79)	18.08(18.01)	6.41(6.48)
E17		<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	60.6 ~ 61.0	46.20	61.68(61.79)	18.10(18.01)	6.39(6.48)
E18		<i>i</i> -C <sub>4</sub> H <sub>9</sub>	76.6 ~ 77.1	42.30	61.83(61.79)	17.97(18.01)	6.56(6.48)
E19		<i>i</i> -C <sub>5</sub> H <sub>11</sub>	83.7 ~ 84.8	75.00	63.02(63.14)	17.03(16.99)	6.85(6.93)
E20		CH <sub>3</sub>	112.2 ~ 112.8	69.30	41.78(41.65)	12.02(12.14)	3.09(3.06)

续表 1 (Continued table 1)

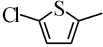
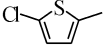
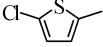
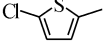
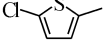
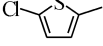
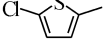
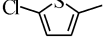
化合物 Compd.	R <sup>1</sup>	R	熔点 m. p. /°C or $n_D^{31}$	收率 Yield/%	元素分析(计算值)/%		
					Elemental analysis(Calcd.)/%		
					C	N	H
<b>E21</b>		C <sub>2</sub> H <sub>5</sub>	76.0 ~ 76.8	72.70	44.29(44.18)	11.31(11.45)	3.63(3.71)
<b>E22</b>		<i>n</i> -C <sub>3</sub> H <sub>7</sub>	66.6 ~ 67.4	66.90	46.30(46.42)	10.92(10.83)	4.21(4.29)
<b>E23</b>		<i>i</i> -C <sub>3</sub> H <sub>7</sub>	84.9 ~ 85.4	58.70	46.53(46.42)	10.75(10.83)	4.26(4.29)
<b>E24</b>		CH <sub>2</sub> CH = CH <sub>2</sub>	78.8 ~ 79.5	63.60	46.64(46.79)	10.97(10.91)	3.45(3.53)
<b>E25</b>		<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> 31D = 1.6572	70.90	48.37(48.44)	10.35(10.27)	4.73(4.80)
<b>E26</b>		<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> 31D = 1.6585	64.30	48.52(48.44)	10.18(10.27)	4.85(4.80)
<b>E27</b>		<i>i</i> -C <sub>4</sub> H <sub>9</sub>	99.5 ~ 100.0	66.70	48.49(48.44)	10.21(10.27)	4.88(4.80)
<b>E28</b>		<i>i</i> -C <sub>5</sub> H <sub>11</sub>	75.2 ~ 76.8	58.20	50.12(50.26)	9.90(9.77)	5.18(5.27)

表 2 化合物 D 和 E 的核磁共振氢谱数据

Table 2 <sup>1</sup>H NMR data of compounds D and E

化合物 Compd.	<sup>1</sup> H NMR (CDCl <sub>3</sub> /TMS), δ
<b>D01</b>	4.74 (s, 2H, OCH <sub>2</sub> ), 6.49 ~ 6.50 (m, 1H, furanylH-4), 6.87 (d, 1H, <i>J</i> = 2.70 Hz, furanylH-3), 7.53 (d, 1H, furanyl H-5, <i>J</i> = 1.75 Hz), 8.59 (s, 1H, NH)
<b>D02</b>	4.82 (s, 2H, OCH <sub>2</sub> ), 7.48 ~ 7.52 (m, 1H, pyridinylH-5), 8.11 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.67 (d, 1H, <i>J</i> = 3.30 Hz, pyridinylH-6), 8.93 (s, 1H, pyridinylH-2), 11.24 (s, 1H, NH)
<b>D03</b>	4.76 (s, 2H, OCH <sub>2</sub> ), 6.89 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.26 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4), 8.32 (s, 1H, NH)
<b>E01</b>	3.40 (s, 3H, CH <sub>3</sub> ), 4.68 (s, 2H, OCH <sub>2</sub> ), 6.48 ~ 6.49 (m, 1H, furanylH-4), 6.85 (d, 1H, <i>J</i> = 3.00 Hz, furanylH-3), 7.53 (d, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
<b>E02</b>	1.28 (t, 3H, <i>J</i> = 7.20 Hz, CH <sub>3</sub> ), 3.80 ~ 3.87 (m, 2H, N - CH <sub>2</sub> ), 4.66 (s, 2H, OCH <sub>2</sub> ), 6.47 ~ 6.49 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.00 Hz, furanylH-3), 7.53 (d, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
<b>E03</b>	0.91 (t, 3H, <i>J</i> = 7.30 Hz, CH <sub>3</sub> ), 1.69 ~ 1.76 (m, 2H, CH <sub>2</sub> ), 3.72 (t, 3H, <i>J</i> = 7.35 Hz, N - CH <sub>2</sub> ), 4.64 (s, 2H, OCH <sub>2</sub> ), 6.47 ~ 6.49 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.60 Hz, furanylH-3), 7.50 (d, 1H, <i>J</i> = 1.75 Hz, furanylH-5)
<b>E04</b>	1.29 (d, 6H, <i>J</i> = 6.90 Hz, CH <sub>3</sub> ), 4.64 (s, 2H, OCH <sub>2</sub> ), 4.86 ~ 4.95 (m, 1H, CH), 6.47 ~ 6.49 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.70 Hz, furanylH-3), 7.52 (d, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
<b>E05</b>	4.38 (d, 2H, <i>J</i> = 5.70 Hz, CH <sub>2</sub> ), 4.69 (s, 2H, OCH <sub>2</sub> ), 5.21 ~ 5.32 (m, 2H, = CH <sub>2</sub> ), 5.86 ~ 5.95 (m, 1H, = CH), 6.46 ~ 6.48 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.70 Hz, furanylH-3), 7.51 (d, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
<b>E06</b>	0.95 (t, 3H, <i>J</i> = 7.20 Hz, CH <sub>3</sub> ), 1.32 ~ 1.40 (m, 2H, CH <sub>2</sub> ), 1.65 ~ 1.73 (m, 2H, CH <sub>2</sub> ), 3.78 (t, 2H, <i>J</i> = 7.35 Hz, N - CH <sub>2</sub> ), 4.67 (s, 2H, OCH <sub>2</sub> ), 6.49 ~ 6.50 (m, 1H, furanylH-4), 6.85 (d, 1H, <i>J</i> = 3.30 Hz, furanylH-3), 7.54 (d, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
<b>E07</b>	0.86 (t, 3H, <i>J</i> = 7.30 Hz, CH <sub>3</sub> ), 1.27 (d, 3H, <i>J</i> = 7.10 Hz, CH <sub>3</sub> ), 1.54 ~ 1.85 (m, 2H, CH <sub>2</sub> ), 4.62 ~ 4.71 (m, 1H, CH), 4.66 (s, 2H, OCH <sub>2</sub> ), 6.47 ~ 6.48 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.30 Hz, furanylH-3), 7.53 (d, 1H, <i>J</i> = 1.90 Hz, furanylH-5)
<b>E08</b>	0.95 (d, 6H, <i>J</i> = 5.10 Hz, CH <sub>3</sub> ), 2.19 ~ 2.21 (m, 1H, CH), 3.61 (d, 2H, <i>J</i> = 6.30 Hz, N - CH <sub>2</sub> ), 4.69 (s, 2H, OCH <sub>2</sub> ), 6.49 ~ 6.51 (m, 1H, furanylH-4), 6.87 (d, 1H, <i>J</i> = 3.40 Hz, furanylH-3), 7.54 (d, 1H, <i>J</i> = 1.70 Hz, furanylH-5)

续表2(Continued table 2)

化合物 Compd.	<sup>1</sup> H NMR (CDCl <sub>3</sub> /TMS), δ
E09	2.44 ~ 2.51 (m, 2H, CH <sub>2</sub> ), 3.85 (t, <i>J</i> = 7.20 Hz, 2H, N - CH <sub>2</sub> ), 4.65 (s, 2H, OCH <sub>2</sub> ), 5.02 ~ 5.13 (m, 2H, = CH <sub>2</sub> ), 5.74 ~ 5.83 (m, 1H, = CH), 6.48 ~ 6.49 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.30 Hz, furanylH-3), 7.53 (d, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
E10	0.93 (d, 6H, <i>J</i> = 6.00 Hz, CH <sub>3</sub> ), 1.58 ~ 1.62 (m, 3H, CH and CH <sub>2</sub> ), 3.78 (t, 2H, <i>J</i> = 7.20 Hz, N - CH <sub>2</sub> ), 4.65 (s, 2H, OCH <sub>2</sub> ), 6.47 ~ 6.49 (m, 1H, furanylH-4), 6.84 (d, 1H, <i>J</i> = 3.00 Hz, furanylH-3), 7.52 (t, 1H, <i>J</i> = 1.80 Hz, furanylH-5)
E11	3.40 (s, 3H, CH <sub>3</sub> ), 4.76 (s, 2H, OCH <sub>2</sub> ), 7.34 ~ 7.38 (m, 1H, pyridinylH-5), 8.15 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.67 (d, 1H, <i>J</i> = 3.30 Hz, pyridinylH-6), 9.06 (s, 1H, pyridinylH-2)
E12	1.30 (t, 3H, <i>J</i> = 7.20 Hz, CH <sub>3</sub> ), 3.81 ~ 3.88 (m, 2H, CH <sub>2</sub> ), 4.74 (s, 2H, OCH <sub>2</sub> ), 7.34 ~ 7.38 (m, 1H, pyridinylH-5), 8.15 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.67 (d, 1H, <i>J</i> = 3.30 Hz, pyridinylH-6), 9.08 (s, 1H, pyridinylH-2)
E13	0.95 (t, 3H, <i>J</i> = 7.35 Hz, CH <sub>3</sub> ), 1.72 ~ 1.79 (m, 2H, CH <sub>2</sub> ), 3.75 (t, 2H, <i>J</i> = 7.20 Hz, N - CH <sub>2</sub> ), 4.75 (s, 2H, OCH <sub>2</sub> ), 7.35 ~ 7.38 (m, 1H, pyridinylH-5), 8.15 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.66 (d, 1H, <i>J</i> = 3.00 Hz, pyridinylH-6), 9.07 (s, 1H, pyridinylH-2)
E14	1.30 (d, 6H, <i>J</i> = 6.60 Hz, CH <sub>3</sub> ), 4.75 (s, 2H, OCH <sub>2</sub> ), 4.91 ~ 5.00 (m, 1H, CH), 7.38 ~ 7.42 (m, 1H, pyridinylH-5), 8.18 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.68 (d, 1H, <i>J</i> = 4.80 Hz, pyridinylH-6), 9.11 (s, 1H, pyridinylH-2)
E15	4.41 (d, 2H, <i>J</i> = 6.00 Hz, CH <sub>2</sub> ), 4.80 (s, 2H, OCH <sub>2</sub> ), 5.26 ~ 5.36 (m, 2H, = CH <sub>2</sub> ), 5.90 ~ 5.99 (m, 1H, = CH), 7.36 ~ 7.40 (m, 1H, pyridinylH-5), 8.15 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.68 (d, 1H, <i>J</i> = 3.60 Hz, pyridinylH-6), 9.08 (s, 1H, pyridinylH-2)
E16	0.96 (t, 3H, <i>J</i> = 7.35 Hz, CH <sub>3</sub> ), 1.35 ~ 1.43 (m, 2H, CH <sub>2</sub> ), 1.67 ~ 1.74 (m, 2H, CH <sub>2</sub> ), 3.80 (t, 2H, <i>J</i> = 7.05 Hz, N - CH <sub>2</sub> ), 4.75 (s, 2H, OCH <sub>2</sub> ), 7.35 ~ 7.39 (m, 1H, pyridinylH-5), 8.15 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.67 (d, 1H, <i>J</i> = 3.30 Hz, pyridinylH-6), 9.08 (s, 1H, pyridinylH-2)
E17	0.90 (t, 3H, <i>J</i> = 7.50 Hz, CH <sub>3</sub> ), 1.29 (d, 3H, <i>J</i> = 6.60 Hz, CH <sub>3</sub> ), 1.57 ~ 1.86 (m, 2H, CH <sub>2</sub> ), 4.67 ~ 4.78 (m, 1H, CH), 4.78 (s, 2H, OCH <sub>2</sub> ), 7.45 ~ 7.49 (m, 1H, pyridinylH-5), 8.25 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.70 (d, 1H, <i>J</i> = 4.50 Hz, pyridinylH-6), 9.12 (s, 1H, pyridinylH-2)
E18	0.98 (d, 6H, <i>J</i> = 5.70 Hz, CH <sub>3</sub> ), 1.59 ~ 1.68 (m, 1H, CH), 3.81 (d, 2H, <i>J</i> = 7.50 Hz, N - CH <sub>2</sub> ), 4.75 (s, 2H, OCH <sub>2</sub> ), 7.36 ~ 7.40 (m, 1H, pyridinylH-5), 8.16 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.69 (d, 1H, <i>J</i> = 4.80 Hz, pyridinylH-6), 9.09 (s, 1H, pyridinylH-2)
E19	0.97 (d, 6H, <i>J</i> = 5.70 Hz, CH <sub>3</sub> ), 1.59 ~ 1.68 (m, 3H, CH and CH <sub>2</sub> ), 3.82 (t, 2H, <i>J</i> = 6.90 Hz, N - CH <sub>2</sub> ), 4.75 (s, 2H, OCH <sub>2</sub> ), 7.36 ~ 7.40 (m, 1H, pyridinylH-5), 8.16 (d, 1H, <i>J</i> = 8.10 Hz, pyridinylH-4), 8.69 (d, 1H, <i>J</i> = 4.80 Hz, pyridinylH-6), 9.09 (s, 1H, pyridinylH-2)
E20	3.35 (s, 3H, CH <sub>3</sub> ), 4.69 (s, 2H, OCH <sub>2</sub> ), 6.87 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.24 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E21	1.30 (t, 3H, <i>J</i> = 7.20 Hz, CH <sub>3</sub> ), 3.78 ~ 3.85 (m, 2H, CH <sub>2</sub> ), 4.70 (s, 2H, OCH <sub>2</sub> ), 6.89 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.26 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E22	0.93 (t, 3H, <i>J</i> = 7.35 Hz, CH <sub>3</sub> ), 1.67 ~ 1.74 (m, 2H, CH <sub>2</sub> ), 3.67 (t, 2H, <i>J</i> = 7.05 Hz, CH <sub>2</sub> ), 4.66 (s, 2H, OCH <sub>2</sub> ), 6.84 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.20 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E23	1.30 (d, 6H, <i>J</i> = 6.60 Hz, CH <sub>3</sub> ), 4.71 (s, 2H, OCH <sub>2</sub> ), 4.91 ~ 4.96 (m, 1H, CH), 6.91 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.27 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E24	4.33 (d, 2H, <i>J</i> = 5.70 Hz, CH <sub>2</sub> ), 4.70 (s, 2H, OCH <sub>2</sub> ), 5.22 ~ 5.32 (m, 2H, = CH <sub>2</sub> ), 5.85 ~ 5.94 (m, 1H, = CH), 6.86 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.23 (d, 1H, <i>J</i> = 4.20 Hz, thiophenylH-4)
E25	0.93 (t, 3H, <i>J</i> = 7.35 Hz, CH <sub>3</sub> ), 1.33 ~ 1.35 (m, 2H, CH <sub>2</sub> ), 1.62 ~ 1.67 (m, 2H, CH <sub>2</sub> ), 3.65 (t, 2H, <i>J</i> = 7.20 Hz, CH <sub>2</sub> ), 4.64 (s, 2H, OCH <sub>2</sub> ), 6.84 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.20 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E26	0.87 (t, 3H, <i>J</i> = 7.35 Hz, CH <sub>3</sub> ), 1.24 (d, 3H, <i>J</i> = 6.60 Hz, CH <sub>3</sub> ), 1.53 ~ 1.77 (m, 2H, CH <sub>2</sub> ), 4.60 ~ 4.68 (m, 3H, CH and OCH <sub>2</sub> ), 6.87 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.22 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E27	0.94 (d, 6H, <i>J</i> = 6.60 Hz, CH <sub>3</sub> ), 2.11 ~ 2.16 (m, 1H, CH), 3.55 (d, 2H, <i>J</i> = 7.20 Hz, CH <sub>2</sub> ), 4.68 (s, 2H, OCH <sub>2</sub> ), 6.87 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.22 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)
E28	0.95 (d, 6H, <i>J</i> = 6.30 Hz, CH <sub>3</sub> ), 1.56 ~ 1.63 (m, 3H, CH and CH <sub>2</sub> ), 3.75 (t, 2H, <i>J</i> = 7.05 Hz, CH <sub>2</sub> ), 4.67 (s, 2H, OCH <sub>2</sub> ), 6.87 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-3), 7.22 (d, 1H, <i>J</i> = 3.90 Hz, thiophenylH-4)

## 2.2 除草活性

测定结果见表3。可以看出,部分化合物对马唐和苋菜具有明显的除草活性。与课题组曾经研究过的2-位上为取代苯基和取代苯乙烯基的化合物比较,可以发现,2-位上取代基不同,表现出的生物活性不同;如为取代苯基时,化合物具有一定的杀菌活性<sup>[3]</sup>;为取代苯乙烯基时,表现出一定的杀虫活

性<sup>[4]</sup>;而本文报道的2-位上为杂环基时,化合物表现出的则是除草活性。除草活性的大小则与4-位的取代基R有一定关系:当R为H时,化合物均无活性;当R为烯丙基时,化合物的活性均小于90%;而当R为供电子基团时,化合物活性均大于90%。此类化合物深入的结构-活性关系值得进一步研究。

表3 部分化合物在200 mg/L下的除草活性(抑制率/%)<sup>\*</sup>

Table 3 Herbicidal activity of some compounds at 200 mg/L (Inhibition rate/%)<sup>\*</sup>

化合物 Compd.	株高/根长 Shoot/Root		化合物 Compd.	株高/根长 Shoot/Root	
	马唐 <i>Digitaria sanguinalis</i>	苋菜 <i>Ambrosia tricolor</i>		马唐 <i>Digitaria sanguinalis</i>	苋菜 <i>Ambrosia tricolor</i>
E02	40/40	65/65	E15	45/30	75/75
E03	50/50	75/75	E16	90/90	90/90
E04	20/20	70/70	E17	50/50	75/75
E05	20/20	75/75	E18	75/75	75/75
E06	75/75	90/90	E19	70/70	75/75
E07	30/30	90/90	E20	95/95	90/90
E08	20/20	75/75	E21	90/90	85/85
E09	35/25	75/75	E22	70/70	60/60
E10	25/20	90/90	E23	10/15	70/70
E12	55/65	65/65	E24	70/70	70/78
E13	50/60	70/75	E25	65/65	30/30
E14	90/90	90/90	E26	5/5	60/60

<sup>\*</sup> 未列出化合物在测试浓度下均无活性。<sup>\*</sup> There is no activity for the unlisted compounds at the tested concentration.

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