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草茎点霉毒素Ⅲ衍生物的合成与除草活性

纪明山, 刘 欣, 高云云, 李兴海*

(沈阳农业大学 植物保护学院,沈阳 110866)

摘 要:为了提高草茎点霉毒素Ⅲ(2-甲基-3,5-二硝基苯甲酸甲酯)的除草活性,对其结构进行衍生优化。以邻甲基苯甲酸为起始原料,经硝化、酯化等反应合成了34个新的苯甲酸酯类化合物,其结构均通过IR、^{1}H NMR和GC-MS确证。杂草种子萌发试验结果表明,目标化合物对供试杂草根的抑制率明显高于茎,在100 μg/mL时,**4-15**、**4-16**和**4-26**对反枝苋*Amaranthus retroflexus*根的抑制率分别为92.8%、92.0%和87.4%,有较显著的除草活性;活体盆栽试验结果表明,在有效成分1 000 g/hm^{2}时,**4-1**对马唐*Digitaria sanguinalis*和反枝苋*A. retroflexus*的鲜重防效均达100%,有较高的除草活性;毒力测定结果表明,**4-1**对马唐*D. sanguinalis*的ED$_{50}$值为有效成分94.89 g/hm^2。

关键词:草茎点霉;苯甲酸酯;合成;除草活性

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Synthesis and herbicidal activity evaluation of toxins Ⅲ from *Phoma herbarbum* derivatives

Ji Mingshan, Liu Xin, Gao Yunyun, Li Xinghai*

(*Plant Protection College*, *Shenyang Agricultural University*, *Shenyang* 110866, *China*)

Abstract: In order to improve the herbicidal activity of toxins Ⅲ(2-methyl-3, 5-dinitrobenzoic acid methyl ester) from *Phoma herbarbum*, their structure were optimized by derivation. 34 novel title compounds were synthesized by nitration, esterification starting from *o-toluic* acid as the starting material. Their structure were characterized by IR, ^{1}H NMR and GC-MS. The screening of the herbicidal activity showed that the inhibition rates of the target compounds on the roots of weed were higher than that of the shoots. The inhibition rates of **4-15**, **4-16** and **4-26** against *Amaranthus retroflexus* root were 92.8%, 92.0% and 87.4% at 100 μg/mL, respectively, which demonstrated significant herbicidal activity. The fresh weight efficacy of **4-1** against *Digitaria sanguinalis* and *A. sretroflexus* was 100% at 1 000 g *a. i.* /hm^2, which illustrated high herbicidal activity. The ED$_{50}$ value for *D. sanguinalis* was 94.89 g *a. i.* /hm^2.

Keywords: *Phoma herbarbum*; benzoic esters; synthesis; herbicidal activity

草茎点霉*Phoma herbarum*是一种分布广泛的植物病原真菌,具有降解植物的特性[1],已经引起国内外学者的广泛关注。Kalam等[2]发现,一种新颖的草茎点霉毒素酚类化合物FGCC#54具有潜在的除草活性。Rivero-Cruz等[3]从蒲公英草茎点霉发酵液的乙酸乙酯提取物中分离得到了

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作者简介:纪明山,男,博士,教授,主要从事农药毒理学研究,**E-mail**:jimingshan@163.com;* 李兴海,通信作者(Author for correspondence),男,博士,副教授,主要从事农药化学与生物活性研究,**E-mail**:xinghai30@163.com

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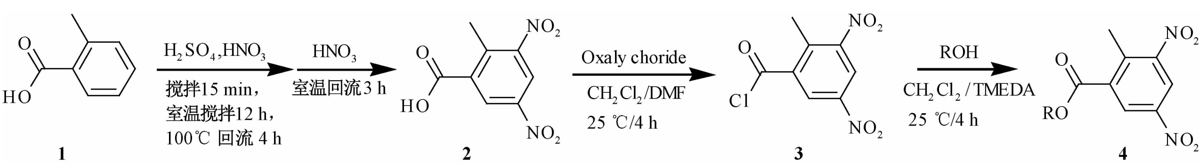
Herbarumin、Herbarumin Ⅱ和 Herbarumin Ⅲ,均属于十元内酯环状化合物,其中 Herbarumin Ⅲ对籽粒苋 *Amaranthus hypochondriacus* 胚根生长的抑制活性是2,4-D 的 10 倍。谷祖敏等[4]从鸭跖草 *Commelina communis* 中分离出了草茎点霉粗毒素,发现其对藜 *Chenopodium album* 和反枝苋 *Amaranthus retroflexus* 有除草活性;李思嘉等[5]对草茎点霉粗毒素Ⅲ进行了分离纯化,并鉴定其为2-甲基-3,5-二硝基苯甲酸甲酯。目前关于羧酸酯类化合物作为除草剂的报道较少,已商品化的主要有嘧啶氧(硫)苯甲酸酯类化合物[6-7]。据文献报道:2-(5,7-二甲基-1,2,4-三唑[1,5-α]-嘧啶-2-基氧基)苯甲酸异丙酯具有很好的除草活性[8];具有高表面渗透性的(2,4-二氯苯氧基)乙酸乙二酯也显示出优异的除草活性[9];CGA 201029/R69020[1-(2,2-二甲基茚满-1-基)咪唑-5-羧酸甲酯]在植物体内能够抑制甾醇生物合成[10];2-([(4-氯-6-甲氧基嘧啶-2-基氧基)酰胺]磺酰胺)苯甲酸乙酯对大豆田和玉米田的杂草有不同的除草活性[11];1,8-桉树脑和1,4-桉树脑酯的衍生物对一年生黑麦草和萝卜具有苗后和苗前除草活性[12-13];4-碘-2-[3-(4-甲氧基-6-甲基-1,3,5-三嗪-2-基)脲磺酰]苯甲酸酯有高除草活性[14]。为了提高草茎点霉毒素Ⅲ(2-甲基-3,5-二硝基苯甲酸甲酯)的除草活性,笔者对其结构进行衍生优化,以邻甲基苯甲酸为起始原料,合成一系列未见文献报道的苯甲酸酯类化合物。通过 ^{1}H NMR、IR 和 GC-MS 对其结构进行了确证,并测定了其对几种杂草的除草活性。合成路线见 **Scheme 1**。



Scheme 1

1　实验部分

1.1　仪器与药剂

WD-9403A 型荧光-紫外分析仪;Spectrum 65 型傅里叶红外光谱仪(KBr 压片法);BRUKER 600 MHz 核磁共振波谱仪(TMS 为内标,$CDCl_3$ 为溶剂 $CDCl_3$);AGILENT 6890-5973N 气相色谱-质谱联用仪。

一元取代醇及其他试剂均为市售分析纯或化学纯,其中一元取代醇经 3A 分子筛脱水处理后使用,二氯甲烷用五氧化二磷干燥,*N*,*N*-二甲基甲酰胺(DMF)和 *N*,*N*,*N*′,*N*′-四甲基乙二胺(TMEDA)经氢化钙回流 2 h 并减压蒸馏后使用。对照药剂为48%莠去津可湿性粉剂(atrazine WP),山东碧奥生物科技有限公司;5%精喹禾灵乳油(quizalofop-*p*-ethyl EC),京博农化科技有限公司;50%乙草胺乳油(acetochlor EC),山东乐邦化学品有限公司。

1.2　供试杂草

稗草 *Echinochloa crusgalli*、牛筋草 *Eleusine indica*、狗尾草 *Setaria viridis*、马唐 *Digitaria sanguinalis*、苘麻 *Abutilon theophrasti*、反枝苋 *Amaranthus retroflexus*、马齿苋 *Portulaca oleracea*、鸭跖草 *Commelina communis* 和藜 *Chenopodium album*,均由沈阳农业大学植物保护学院农药科学教研室采集、保存。

1.3　化合物的合成

1.3.1　化合物 **2**　按照文献[15]方法合成。

1.3.2　化合物 **4**　按照文献[16-17]方法合成。

1.4　除草活性测定

1.4.1　种子萌发试验

1.4.1.1　除草活性初筛　参考文献[12]方法。供试化合物先用丙酮溶解后,再用 0.34 mg/mL 的吐温-20 水溶液配制成 500 μg/mL 的供试化合物溶液。移取 1 mL 供试化合物溶液于滤纸上,放入 10 粒大小均匀、刚露白的杂草种子,用保鲜膜密封,置于 25 ℃的培养箱中光照培养 72 h,测量杂草种子的根与茎长度。每处理重复 3 次。以 0.34 mg/mL 的吐温-20 水溶液作空白对照,50%乙草胺乳油为药剂对照。按式(1)计算化合物对杂草胚根和茎的平均抑制率。

$$\text{抑制率}/\% = \frac{\text{空白平均长度} - \text{处理平均长度}}{\text{空白平均长度}} \times 100 \quad (1)$$

除草活性分级标准[18]:A 级,抑制率≥90%;B 级,抑制率≥70%;C 级,抑制率≥50%;D 级,抑制率<50%。

1.4.1.2　除草活性复筛　以 50%乙草胺乳油为对照药剂,对初筛活性较好的化合物进行复筛。分别

设置100 和20 μg/mL 两个质量浓度。试验方法同1.4.1.1 节。

1.4.2 活体盆栽试验

1.4.2.1 除草活性初筛 参考文献[19]方法。供试化合物先用丙酮溶解,再用0.34 mg/mL 的吐温-20 水溶液配制成有效成分1 000 g/hm^2 的供试溶液。以0.34 mg/mL 的吐温-20 水溶液和丙酮混合液作空白对照,以5% 精喹禾灵乳油和48% 莠去津可湿性粉剂为药剂对照。将供试土壤装至盆钵4/5 处,播种15 ~20 粒杂草种子,根据种子大小覆土0.5 ~2 cm。以盆钵底部渗灌方式浇水,使土壤完全湿润后移入温室进行常规培养(白天25 ℃ ±5 ℃,夜间14 ℃ ±5 ℃)。杂草出苗后间苗定株(总密度120 ~150 株/m^2)。在杂草长至2 ~4 叶期进行药剂喷雾处理,喷雾量为有效成分1 000 g/hm^2,待植株表面药液自然风干后,移至温室常规培养,定期观察记载杂草生长状态。每处理重复3 次。处理14 d 后,采用绝对值法调查化合物对杂草的影响,按(2)式计算杂草鲜重防效(E_f)。

$$E_f/\% = \frac{m_c - m_t}{m_c} \times 100 \quad (2)$$

式中:m_c—对照杂草地上部分鲜重;m_t—处理杂草地上部分鲜重。

1.4.2.2 除草活性复筛 对初筛中鲜重防效达到90% 的化合物进行复筛,设计药剂喷雾量为有效成分62.5 ~1 000 g/hm^2,试验方法同1.4.2.1 节。

2 结果与讨论

2.1 化合物的合成

目标化合物的收率、理化性质及质谱数据见表1;^{1}H NMR 及IR 数据见表2。谱图数据与化合物结构吻合较好。在合成目标化合物**4** 时,曾尝试直接由化合物**2** 通过浓硫酸催化与醇发生酯化反应得到,但收率较低,因此改用酰氯和醇反应,产物较易纯化,收率较高。

表1 目标化合物的理化数据及质谱数据

Table 1 Physicochemical and GC-MS data of target compounds

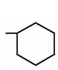
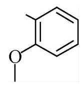
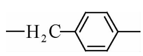
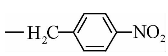
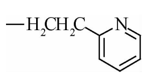
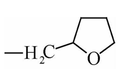
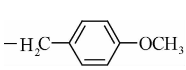
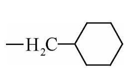
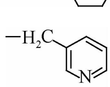
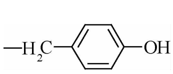
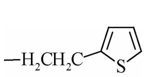
化合物 Compd.	R	收率 Yield/%	物态(室温) State(r. t.)	熔点 m. p. /℃(Lit.)	质谱 MS 分子离子峰(m/z)
4-1	$—CH_2CH_3$	82.0	淡黄色液体 Pale yellow liquid	–	254(M$^+$),225,209,105
4-2	$—CH(CH_3)_2$	76.4	淡黄色液体 Pale yellow liquid	–	269[M+H]$^+$,226,209,105
4-3	$—(CH_2)_3CH_3$	86.5	淡黄色液体 Pale yellow liquid	–	282(M$^+$),226,209,105
4-4	$—(CH_2)_4CH_3$	74.9	淡黄色液体 Pale yellow liquid	–	297[M+H]$^+$,226,209,105
4-5	$—CH_2CH_2CH(CH_3)_2$	88.0	淡黄色液体 Pale yellow liquid	–	297[M+H]$^+$,226,209,105
4-6	$—(CH_2)_5CH_3$	89.8	淡黄色液体 Pale yellow liquid	–	311[M+H]$^+$,226. 209,105
4-7	$—(CH_2)_6CH_3$	93.1	淡黄色液体 Pale yellow liquid	–	325[M+H]$^+$,226,209
4-8		90.0	淡黄色液体 Pale yellow liquid	–	309[M+H]$^+$,226,209,105
4-9	$—(CH_2)_7CH_3$	87.0	淡黄色液体 Pale yellow liquid	–	339[M+H]$^+$,226,209
4-10	$—CH_2C_6H_5$	87.0	淡黄色粉末 Pale yellow powder	67.0 ~69.0	316(M$^+$),209,107
4-11	$—(CH_2)_9CH_3$	69.8	淡黄色液体 Pale yellow liquid	–	367[M+H]$^+$,226,209
4-12	$—CH_2CH(CH_3)CH_2CH_3$	66.5	淡黄色液体 Pale yellow liquid	–	297[M+H]$^+$,226,209,105
4-13	$—CH_2CH(CH_2CH_3)_2$	68.7	淡黄色液体 Pale yellow liquid	–	311[M+H]$^+$,226,209,105
4-14	$—C_6H_5$	90.2	红色粉末 Red powder	94.6 ~97.7	302(M$^+$),225,209,105

表 1(续表)

Table 1(Continued)

化合物 Compd.	R	收率 Yield/%	物态(室温) State(r. t.)	熔点 m. p. /℃(Lit.)	质谱 MS 分子离子峰(*m/z*)
4-15		89.5	红色粉末 Red powder	127.4 ~ 128.3	332(M^+),225,209,105
4-16	$-CH_2CF_3$	74.7	淡黄色晶体 Pale yellow crystalline	77.9 ~ 79.4	308(M^+),225,209,105
4-17		96.4	淡黄色晶体 Pale yellow crystalline	85.0 ~ 87.6	330(M +),209,105
4-18	$-CH(CH_2Cl)_2$	80.1	黄色晶体 Yellow crystalline	91.1 ~ 93.8	336$[M+H]^+$,225,209
4-19	$-CH_2CH{=}C(CH_3)_2$	89.0	黄色液体 Yellow liquid	–	294(M^+),209,105
4-20		89.8	淡黄色晶体 Pale yellow crystalline	116 ~ 117.9	361(M^+),225,209
4-21	$-(CH_2)_3Cl$	93.4	黄色液体 Yellow liquid	–	301$[M\text{-}H]^+$,225,209,105
4-22	$-CH_2CH{=}CHC_6H_5$	92.3	淡黄色粉末 Pale yellow powder	77.4 ~ 77.6	381$[M+Na]^+$,225,109,133
4-23		93.5	淡黄色粉末 Pale yellow powder	75.2 ~ 76.4	233,121
4-24		97.0	淡黄色粉末 Pale yellow powder	73.5 ~ 76.0	309$[M\text{-}H]^+$,225,209,105
4-25		90.0	淡黄色液体 Pale yellow liquid	–	346(M^+),225,121,109
4-26	$-CH_2CH_2OCH{=}CH_2$	76.3	淡黄色液体 Pale yellow liquid	–	296(M^+),209,105
4-27	$-(CH_2)_2OCH_2C_6H_5$	68.2	淡黄色液体 Pale yellow liquid	–	360(M^+),209
4-28	$-(CH_2)_6Cl$	72.3	淡黄色液体 Pale yellow liquid	–	344(M^+),226,209,105
4-29		51.2	淡黄色液体 Pale yellow liquid	–	323$[M+H]^+$,226,209,105
4-30		83.0	淡黄色晶体 Pale yellow crystalline	66.5 ~ 67.4	316$[M\text{-}H]^+$,225,209,92
4-31	$-C(CH_3)_2C{\equiv}CH$	62.0	淡黄色晶体 Pale yellow crystalline	78.5 ~ 80.5	292(M^+),209,105
4-32		82.0	白色粉末 White powder	163.5 ~ 165.9	331$[M\text{-}H]^+$,209,106
4-33		86.1	淡黄色晶体 Pale yellow crystalline	71.5 ~ 72.6	336(M^+),225,209,110,98
4-34	$-(CH_2)_3Br$	88.8	白色晶体 White crystalline	52.0 ~ 53.3	225,209,121,105

注:"–"无试验数据。Note:"–",No data.

2.2　除草活性

2.2.1　种子萌发试验结果　除草活性初筛结果(表 3)表明:在药剂质量浓度为 500 μg/mL 时,目标化合物对双子叶杂草的除草活性明显高于单子叶杂草,对根的抑制效果高于茎,尤其对反枝苋的抑制效果最好,其中 **4-15**、**4-16** 和 **4-26** 对反枝苋的抑制效果达到 100%,有较高的除草活性。**4-1** 和 **4-2** 对双子叶杂草和单子叶杂草均有很好的除草活性,抑制效果基本达到 B 级。在所有的单子叶杂草中,化合物对牛筋草更为敏感。对初筛中抑制效果达到 B

级的化合物进行复筛,结果(表4)表明,随着化合物质量浓度的增大,除草活性呈上升趋势,其中**4-15**、**4-16**和**4-26**对反枝苋的除草活性明显高于其他目标化合物。

表2 目标化合物的核磁共振氢谱及红外光谱数据

Table 2 ^{1}H NMR and IR data of target compounds

化合物 Compd.	^{1}H NMR (CDCl$_3$, 600 MHz 或 400 MHz, TMS), δ	IR, ν(C=O)/cm^{-1}
4-1	1.46(t, 3H, J = 6.0 Hz, CH$_3$), 2.75(s, 3H, ArCH$_3$), 4.49 ~ 4.61(q, 2H, J = 6.0 Hz, ArCOOCH$_2$), 8.69(s, 1H, ArH), 8.97(s, 1H, ArH)	1 728
4-2	1.43(d, 6H, J=6.0 Hz, 2CH$_3$), 2.73(s, 3H, ArCH$_3$), 4.10 ~ 4.13(m, 1H, ArCOOCH), 8.68(s, 1H, ArH), 8.78(s, 1H, ArH)	1 720
4-3	1.01(t, 3H, J=8.0 Hz, CH$_3$), 1.47 ~ 1.83(m, 4H, 2CH$_2$), 2.75(s, 3H, ArCH$_3$), 4.42(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 727
4-4	0.94(t, 3H, J=6.0 Hz, CH$_3$), 1.42 ~ 1.84(m, 6H, 3CH$_2$), 2.74(s, 3H, ArCH$_3$), 4.41(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 730
4-5	0.99 ~ 1.05(m, 6H, 2CH$_3$), 1.33 ~ 1.70(m, 1H, CH), 1.70 ~ 1.73(m, 2H, CH$_2$), 2.75(s, 3H, ArCH$_3$), 4.44(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.80(s, 1H, ArH)	1 730
4-6	0.91(s, 3H, CH$_3$), 1.35 ~ 1.45(m, 6H, 3CH$_2$), 1.79 ~ 1.82(m, 2H, CH$_2$), 2.75(s, 3H, ArCH$_3$), 4.40(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 731
4-7	0.90(s, 3H, CH$_3$), 1.31 ~ 1.82(m, 10H, 5CH$_2$), 2.75(s, 3H, ArCH$_3$), 4.40(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 732
4-8	1.33 ~ 1.45(m, 1H, ArCOOCH), 1.48 ~ 1.62(m, 6H, 3CH$_2$), 1.80 ~ 2.02(m, 4H, 2CH$_2$), 2.74(s, 3H, ArCH$_3$), 8.67(s, 1H, ArH), 8.77(s, 1H, ArH)	1 728
4-9	0.88(s, 3H, CH$_3$), 1.33 ~ 1.44(m, 10H, 5CH$_2$), 1.79 ~ 1.83(m, 2H, CH$_2$), 2.74(s, 3H, ArCH$_3$), 4.40(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 732
4-10	2.73(s, 3H, ArCH$_3$), 5.42(s, 2H, ArCOOCH$_2$), 7.40 ~ 7.44(m, 5H, 5ArH), 8.67(s, 1H, ArH), 8.82(s, 1H, ArH)	1 729
4-11	0.88(s, 3H, CH$_3$), 1.36 ~ 1.42(m, 16H, 8CH$_2$), 2.75(s, 3H, ArCH$_3$), 4.40(t, 2H, J=6.6 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 729
4-12	1.03 ~ 1.05(m, 6H, 2CH$_3$), 1.26 ~ 1.56(m, 2H, CH$_2$), 1.87 ~ 1.95(m, 1H, CH), 2.75(s, 3H, ArCH$_3$), 4.20 ~ 4.33(m, 2H, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.81(s, 1H, ArH)	1 728
4-13	0.97(t, 6H, J=7.4 Hz, 2CH$_3$), 1.43 ~ 1.50(m, 4H, 2CH$_2$), 1.69 ~ 1.72(m, 1H, CH), 2.75(s, 3H, ArCH$_3$), 4.35(d, 2H, J=6.0 Hz, ArCOOCH$_2$), 8.68(s, 1H, ArH), 8.80(s, 1H, ArH)	1 732
4-14	2.83(s, 3H, ArCH$_3$), 7.23 ~ 7.50(m, 5H, 5ArCOOArH), 8.74(s, 1H, ArH), 9.08(s, 1H, ArH)	1 747
4-15	2.83(s, 3H, ArCH$_3$), 3.87(s, 3H, ArOCH$_3$), 7.01 ~ 7.33(m, 4H, 4ArCOOArH), 8.74(s, 1H, ArH), 9.07(s, 1H, ArH)	1 761
4-16	2.68(s, 3H, ArCH$_3$), 4.78 ~ 4.82(m, 2H, CH$_2$), 8.75(d, 1H, J=2.4 Hz, ArH), 8.89(d, 1H, J=2.4 Hz, ArH)	1 752
4-17	2.39(s, 3H, ArCH$_3$), 2.73(s, 3H, ArCH$_3$), 5.40(s, 2H, ArCOOCH$_2$), 7.23 ~ 7.37(m, 4H, 4ArH), 8.67(d, 1H, J=2.4 Hz, ArH), 8.82(d, 1H, J=2.4 Hz, ArH)	1 729
4-18	2.78(s, 3H, ArCH$_3$), 3.89 ~ 3.95(m, 4H, 2CH$_2$Cl), 5.50 ~ 5.53(m, 1H, ArCOOCH), 8.73(d, 1H, J=2.4 Hz, ArH), 8.89(d, 1H, J=2.4 Hz, ArH)	1 740
4-19	1.81(d, 6H, J=3.0 Hz, 2CH$_3$), 2.74(s, 3H, ArCH$_3$), 4.89(d, 2H, J=7.2 Hz, ArCOOCH$_2$), 5.47 ~ 5.49(m, 1H, CH═C), 8.67(d, 1H, J=2.4 Hz, ArH), 8.81(d, 1H, J=2.4 Hz, ArH)	1 729
4-20	2.76(s, 3H, ArCH$_3$), 5.53(s, 2H, ArCOOCH$_2$), 7.65(d, 2H, J=2.4 Hz, 2ArH), 8.29(d, 2H, J=2.4 Hz, 2ArH), 8.71(d, 1H, J=2.4 Hz, ArH), 8.88(d, 1H, J=1.8 Hz, ArH)	1 729
4-21	2.28 ~ 2.32(m, 2H, CH$_2$), 2.76(s, 3H, ArCH$_3$), 3.71(t, 2H, J=6.0 Hz, ArCOOCH$_2$), 4.59(t, 2H, J=6.0 Hz, CH$_2$Cl), 8.70(d, 1H, J=2.4 Hz, ArH), 8.82(d, 1H, J=1.8 Hz, ArH)	1 733
4-22	2.78(s, 3H, ArCH$_3$), 5.05 ~ 5.07(m, 2H, ArCOOCH$_2$), 6.39 ~ 6.43(m, 1H, CH=), 6.81(d, 1H, J=15.6 Hz, ArCH=), 7.30 ~ 7.45(m, 5H, 5ArH), 8.70(d, 1H, J=2.4 Hz, ArH), 8.88(d, 1H, J=2.4 Hz, ArH)	1 715

表 2(续表)

Table 2(Continued)

化合物 Compd.	^{1}H NMR (CDCl$_3$, 600 MHz 或 400 MHz, TMS), δ	IR, ν(C=O)/cm^{-1}
4-23	2.65(s, 3H, ArCH$_3$), 3.29(t, 2H, J=6.0 Hz, PyCH$_2$), 4.82(t, 2H, J=6.0 Hz, ArCOOCH$_2$), 7.21~7.27(m, 2H, 2PyH), 7.67~7.70(m, 1H, PyH), 8.61(d, 1H, J=1.8 Hz, PyH), 8.65(d, 1H, J=2.4 Hz, ArH), 8.71(d, 1H, J=2.4 Hz, ArH)	1 734
4-24	1.67~2.02(m, 4H, 2THFCH$_2$), 3.83~3.97(m, 2H, THFCH$_2$), 4.25~4.32(m, 1H, THFH), 4.35~4.51(m, 2H, ArCOOCH$_2$THF), 8.69(d, 1H, J=2.4 Hz, ArH), 8.84(d, 1H, J=2.4 Hz, ArH)	1 728
4-25	2.72(s, 3H, ArCH$_3$), 3.84(s, 3H, ArOCH$_3$), 5.37(s, 2H, ArCOOCH$_2$-Ar), 6.93~6.96(m, 2H, 2ArH), 7.40~7.44(m, 2H, 2ArH), 8.67(d, 1H, J=2.4 Hz, ArH), 8.80(d, 1H, J=2.4 Hz, ArH)	1 722
4-26	2.76(s, 3H, ArCH$_3$), 4.05~4.06(m, 2H, ArCOOCH$_2$), 4.12~4.28(m, 2H, CH$_2$O), 4.65~4.66(m, 2H, =CH$_2$), 6.49~6.53(m, 1H, CH=), 8.70(d, 1H, J=2.4 Hz, ArH), 8.85(d, 1H, J=2.4 Hz, ArH)	1 731
4-27	2.74(s, 3H, ArCH$_3$), 3.83~3.84(m, 2H, CH$_2$O), 4.58~4.60(m, 2H, ArCOOCH$_2$), 4.61(s, 2H, ArCH$_2$), 7.30~7.38(m, 5H, 5ArH), 8.70(d, 1H, J=2.4 Hz, ArH), 8.85(d, 1H, J=2.4 Hz, ArH)	1 731
4-28	1.48~1.57(m, 4H, 2CH$_2$), 1.79~1.87(m, 4H, 2CH$_2$), 2.76(s, 3H, Ar-CH$_3$), 3.55~3.58(m, 2H, CH$_2$Cl), 4.40~4.43(m, 2H, ArCOOCH$_2$), 8.69(d, 1H, J=2.4 Hz, ArH), 8.82(d, 1H, J=2.4 Hz, ArH)	1 729
4-29	1.07~1.09(m, 2H, CH$_2$), 1.20~1.25(m, 1H, CH), 1.28~1.32(m, 2H, CH$_2$), 1.72~1.85(m, 6H, 3CH$_2$), 2.76(s, 3H, ArCH$_3$), 4.22(d, 2H, J=6.0 Hz, ArCOOCH$_2$), 8.69(d, 1H, J=2.4 Hz, ArH), 8.81(d, 1H, J=2.4 Hz, ArH)	1 728
4-30	2.77(s, 3H, ArCH$_3$), 5.54(s, 2H, ArCOOCH$_2$Py), 7.30~7.32(m, 1H, PyH), 7.43(d, 1H, J=6.0 Hz, PyH), 7.76~7.79(m, 1H, PyH), 8.65(d, 1H, J=4.2 Hz, PyH), 8.70(d, 1H, J=2.4 Hz, ArH), 9.06(d, 1H, J=2.4 Hz, ArH)	1 744
4-31	1.87(s, 6H, 2CH$_3$), 2.68(s, 1H, ≡CH), 2.75(s, 3H, ArCH$_3$), 8.69(d, 1H, J=2.4 Hz, ArH), 8.75(d, 1H, J=2.4 Hz, ArH)	1 732
4-32	2.18(s, 1H, ArOH), 2.85(s, 3H, ArCH$_3$), 5.28(s, 2H, ArCOOCH$_2$), 7.32~7.61(m, 4H, 4ArH), 8.71(d, 1H, J=2.4 Hz, ArH), 8.78(d, 1H, J=2.4 Hz, ArH)	1 727
4-33	2.70(s, 3H, ArCH$_3$), 3.34~3.37(m, 2H, ArCH$_2$Th), 4.64(t, 2H, J=6.0 Hz, ArCOOCH$_2$), 6.94~7.23(m, 3H, 3ThH), 8.69(d, 1H, J=2.4 Hz, ArH), 8.82(d, 1H, J=2.4 Hz, ArH)	1 731
4-34	2.36~2.40(m, 2H, CH$_2$), 2.77(s, 3H, ArCH$_3$), 3.55(t, 2H, J=6.0 Hz, CH$_2$Br), 4.58(t, 2H, J=6.0 Hz, ArCOOCH$_2$), 8.71(d, 1H, J=2.4 Hz, ArH), 8.83(d, 1H, J=2.4 Hz, ArH)	1 722

表 3 目标化合物的除草活性

Table 3 The herbicidal activity of target compounds

化合物 Compd.	生长抑制率 Inhibition rate/%													
	苘麻 *A. theophrasti*		反枝苋 *A. retroflexus*		马齿苋 *P. oleracea*		稗草 *E. crusgalli*		马唐 *D. sanguinalis*		狗尾草 *S. viridis*		牛筋草 *E. indica*	
	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot
4-1	90.0	82.5	89.0	68.7	86.9	74.0	87.8	65.7	84.4	83.2	34.6	73.1	89.1	80.9
4-2	86.3	81.5	86.9	68.7	93.4	86.3	83.4	64.5	85.5	84.9	78.2	67.4	96.2	79.2
4-3	44.7	70.4	86.3	54.0	71.0	45.4	43.7	52.9	61.6	65.5	50.5	43.3	86.4	71.0
4-4	36.8	77.2	66.0	30.9	66.1	60.5	20.9	39.1	32.6	20.2	5.3	23.6	84.7	40.4
4-5	25.5	61.5	59.7	22.0	17.9	67.2	47.8	4.5	34.8	60.1	1.1	14.4	74.7	43.7
4-6	32.4	44.8	75.6	28.2	7.1	65.7	8.3	2.0	31.8	41.7	4.8	7.2	62.1	61.2
4-7	4.3	39.9	78.9	30.4	9.5	62.1	68.4	13.6	33.4	−0.8	39.0	12.6	42.0	67.8

表 3(续表)

Table 3(Continued)

化合物 Compd.	生长抑制率 Inhibition rate/% 苘麻 *A. theophrasti*		反枝苋 *A. retroflexus*		马齿苋 *P. oleracea*		稗草 *E. crusgalli*		马唐 *D. sanguinalis*		狗尾草 *S. viridis*		牛筋草 *E. indica*	
	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot
4-8	20.6	63.7	74.5	48.4	3.6	47.5	37.4	7.1	10.6	44.1	3.7	−0.3	62.1	68.3
4-9	12.4	3.3	63.8	37.6	6.0	49.0	7.9	5.9	7.5	5.7	5.9	−8.1	46.9	66.1
4-10	28.6	66.5	75.9	42.4	21.0	29.9	12.4	15.6	41.6	23.6	4.8	11.8	80.1	77.1
4-11	0.2	54.4	32.3	23.6	3.6	56.6	30.2	7.6	55.3	29.1	8.0	14.6	69.5	63.8
4-12	10.9	32.5	86.9	63.5	2.4	60.1	66.2	15.5	67.4	74.1	50.7	22.8	76.3	63.4
4-13	42.4	70.7	28.0	36.3	38.7	43.0	34.5	46.2	46.0	65.6	20.7	36.9	80.1	59.0
4-14	43.0	64.5	28.2	3.8	7.3	37.2	36.9	42.4	47.9	29.3	33.3	41.4	81.5	64.5
4-15	21.5	61.9	100	78.2	15.3	9.9	29.3	19.0	54.0	6.1	9.6	28.7	63.7	64.7
4-16	36.3	54.4	100	89.0	27.4	27.1	52.3	32.6	79.2	31.4	66.9	30.2	79.0	62.8
4-17	38.4	35.3	67.7	14.7	1.6	33.1	26.7	23.8	66.4	14.2	52.9	14.2	43.3	51.9
4-18	29.9	57.0	76.1	66.3	33.3	55.1	50.0	−4.1	72.9	45.7	76.3	43.8	94.3	76.5
4-19	54.3	75.4	78.4	32.5	54.8	51.7	60.3	25.9	52.9	54.2	32.4	20.0	82.0	46.4
4-20	38.4	64.6	62.0	50.7	84.7	50.0	52.9	22.3	45.2	0.4	21.8	7.4	37.6	1.9
4-21	51.0	78.0	66.6	56.7	75.8	53.5	80.4	6.2	54.9	32.7	30.31	−0.5	87.7	73.8
4-22	42.3	66.6	58.4	0.5	69.4	29.7	66.7	18.6	59.5	45.5	59.6	49.6	6.3	23.8
4-23	42.5	62.2	79.7	57.0	75.0	60.1	71.1	70.8	50.1	11.0	68.4	48.8	49.5	43.4
4-24	93.5	90.5	76.4	44.8	44.6	39.8	66.7	8.6	64.3	4.3	78.2	43.5	24.5	23.8
4-25	11.4	43.4	82.2	33.8	6.0	26.8	42.1	2.1	58.4	4.1	10.6	34.6	57.5	67.2
4-26	19.1	60.0	100	56.4	44.8	39.9	45.9	−1.5	35.1	23.8	11.7	−13.1	83.4	41.5
4-27	0.2	22.8	73.4	60.9	3.6	32.4	44.2	8.1	85.8	78.3	18.1	−13.3	35.4	31.1
4-28	46.5	30.9	55.6	26.4	16.7	40.4	51.2	51.2	21.2	60.4	5.3	−6.7	74.4	47.0
4-29	43.4	40.8	52.6	10.8	4.8	63.7	30.6	−0.8	64.6	66.7	−0.5	−4.9	91.8	49.2
4-30	37.4	37.5	65.9	45.3	57.1	46.5	67.2	0.1	65.1	32.1	48.9	21.3	58.2	28.8
4-31	32.7	56.8	50.3	62.7	38.7	40.1	33.4	47.6	55.5	22.0	55.9	38.7	47.7	36.7
4-32	14.8	60.0	68.4	68.5	3.6	60.6	34.6	6.2	30.5	13.8	27.6	10.3	22.1	51.4
4-33	85.0	92.1	48.1	36.0	54.6	14.7	25.9	2.8	67.7	1.0	22.8	1.6	9.9	32.3
4-34	30.6	55.8	45.8	28.0	52.1	5.0	41.8	3.9	67.8	3.3	10.6	−0.5	3.8	16.8
4-0 *	76.3	37.9	82.5	48.6	68.7	24.5	36.2	2.6	44.4	2.7	67.6	−0.9	86.9	32.5
乙草胺 acetochlor	100	100	100	100	100	100	100	100	100	100	100	100	100	100

注(Note):* **4-0**—*Phoma herbarum* Ⅲ。

2.2.2 活体盆栽试验结果 对单、双子叶杂草盆栽苗后茎叶处理试验结果(表 5)表明:部分目标化合物对供试杂草具有一定的除草活性,其中 **4-1** 在有效成分1 000 g/hm^2 下对反枝苋和马唐的鲜重防效达100%。茎叶喷雾处理后第 2 天,杂草的叶片呈水渍状,继而停止生长,10 d 左右死亡。对 **4-1** 进行复筛,结果(表 6)表明,其对双子叶和单子叶杂草仍表现出较高的除草活性,对马唐和反枝苋的 ED_{50} 值均小于100 g/hm^2。

初步构效关系分析发现,在种子萌发试验中,当目标化合物的取代基中含有氟原子时有利于除草活性的提高,如 **4-1** 与 **4-16**。由于氟原子具有模拟效

表 4 部分化合物在不同浓度下的除草活性(抑制率/%)

Table 4 The herbicidal activity of some compounds under different concentration (Inhibition rate/%)

化合物 Compd.	Conc./(mg/L)	苘麻 *A. theophrasti*		反枝苋 *A. retroflexus*		马齿苋 *P. oleracea*		马唐 *D. sanguinalis*		牛筋草 *E. indica*		稗草 *E. crusgalli*		狗尾草 *S. viridis*	
		根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot	根 Root	茎 Shoot
4-1	100	59.3	70.7	81.3	61.8	67.1	46.3	78.5	80.1	84.7	60.3	86.0	56.6	15.4	58.6
	20	47.6	47.7	75.5	58.8	61.5	40.6	57.1	61.1	75.8	35.1	85.7	50.8	8.63	52.3
4-2	100	34.3	54.0	79.4	67.7	64.3	66.6	77.8	69.0	89.7	65.7	80.4	50.8	76.6	66.0
	20	23.1	38.4	72.4	62.4	60.1	58.1	66.9	64.4	85.0	58.5	70.9	28.8	73.8	62.0
4-3	100	23.1	68.8	68.4	53.9	40.5	40.1	–	–	67.8	70.8	–	–	–	–
	20	2.9	29.8	50.7	21.0	36.3	22.0	–	–	64.2	68.1	–	–	–	–
4-4	100	13.0	39.1	–	–	–	–	–	–	69.8	39.6	–	–	–	–
	20	5.7	1.3	–	–	–	–	–	–	50.6	6.30	–	–	–	–
4-5	100	–	–	–	–	–	–	–	–	59.2	37.9	–	–	–	–
	20	–	–	–	–	–	–	–	–	56.5	14.7	–	–	–	–
4-12	100	–	–	78.2	63.4	–	–	60.8	44.2	49.4	36.0	–	–	–	–
	20	–	–	35.8	42.4	–	–	62.0	28.9	26.9	15.1	–	–	–	–
4-13	100	40.4	54.4	–	–	–	–	–	–	63.7	54.9	–	–	–	–
	20	25.0	38.8	–	–	–	–	–	–	48.1	25.3	–	–	–	–
4-15	100	–	–	92.8	65.2	–	–	–	–	–	–	–	–	–	–
	20	–	–	66.6	34.5	–	–	–	–	–	–	–	–	–	–
4-16	100	–	–	92.0	79.8	–	–	72.2	34.2	79.2	60.4	–	–	–	–
	20	–	–	71.0	73.4	–	–	53.1	23.3	72.2	49.6	–	–	–	–
4-18	100	–	–	69.6	61.6	–	–	–	–	–	–	–	–	–	–
	20	–	–	41.1	27.1	–	–	–	–	–	–	–	–	–	–
4-19	100	29.7	66.6	52.8	15.8	–	–	–	–	67.2	35.2	–	–	–	–
	20	12.0	62.5	36.3	3.8	–	–	–	–	56.8	14.1	–	–	–	–
4-21	100	30.5	65.3	–	–	55.2	30.5	–	–	76.1	37.5	62.3	4.5	–	–
	20	25.6	37.6	–	–	39.8	7.9	–	–	52.5	24.4	42.8	3.2	–	–
4-23	100	–	–	65.5	21.9	40.5	17.5	–	–	–	–	63.0	63.9	–	–
	20	–	–	43.0	18.1	30.7	15.8	–	–	–	–	53.7	41.0	–	–
4-26	100	–	–	87.4	38.9	–	–	–	–	70.0	28.3	–	–	–	–
	20	–	–	56.2	15.8	–	–	–	–	69.2	12.7	–	–	–	–
乙草胺 acetochlor	100	100	100	100	100	100	100	100	100	100	100	92.8	88.9	92.8	86.9
	20	67.5	78.8	86.7	46.3	76.8	57.5	67.5	56.5	62.8	62.5	56.6	68.6	68.6	45.8

注:" – ", 无试验数据。Note:" – ",No data.

应、电子效应、阻碍效应和渗透效应,因此,将其引入可能使化合物的生物活性倍增[20]。活体盆栽试验结果表明,目标化合物中 R 基团碳链的长短可影响其除草活性,其中 R 基团碳链越短,除草活性越高。这可能与分子脂溶性有关,一般脂溶性越好,细胞膜渗透性越高,越易被植物吸收。

本研究结果表明:不同目标化合物对于不同杂草的除草活性存在较大差异,且其在种子萌发试验和活体盆栽试验中表现出的除草活性也不尽相同。如在种子萌发试验中 **4-15**、**4-16** 和 **4-26** 对反枝苋有较高的除草活性,但在活体盆栽试验中结果并不理想。这可能是由于在活体盆栽试验中,药剂并未完全吸附在杂草的叶片上,而是有部分流失,结果使其测定结果不及种子萌发试验。总体而言,化合物 **4-1**、**4-15**、**4-16** 和 **4-26** 的除草活性尤为显著,有进一步研究的价值。

表 5 有效成分 1 000 g/hm² 下目标化合物对杂草的鲜重防效

Table 5 The fresh weight efficacy of target compounds against weeds at 1 000 g *a. i.* /hm^2

化合物 Compd.	鲜重防效 Fresh weight efficacy/%						
	苘麻 *A. theophrasti*	反枝苋 *A. retroflexus*	藜 *C. album*	鸭跖草 *C. communis*	狗尾草 *S. viridis*	马唐 *D. sanguinalis*	稗草 *E. crusgalli*
4-1	94	100	99	50	98	100	82
4-2	86	76	82	10	78	87	40
4-3	32	56	23	0	27	78	46
4-4	45	80	75	0	76	38	45
4-5	13	32	46	8	56	78	0
4-6	38	68	0	12	76	32	0
4-7	23	54	10	0	56	32	0
4-8	0	32	35	0	78	68	53
4-9	0	85	80	34	34	54	45
4-10	0	89	85	0	0	83	0
4-11	8	35	78	0	56	75	56
4-12	0	76	0	0	55	70	0
4-13	0	35	0	3	87	0	34
4-14	16	62	0	8	67	78	22
4-15	62	89	32	15	39	35	0
4-16	45	0	54	0	0	40	20
4-17	0	43	36	0	25	35	80
4-18	56	36	78	0	76	25	0
4-19	12	82	35	0	0	0	67
4-20	32	62	50	0	0	12	45
4-21	30	70	65	56	67	56	0
4-22	60	0	75	34	54	48	0
4-23	75	50	0	51	28	38	0
4-24	0	50	35	0	36	44	43
4-25	86	25	46	23	0	36	28
4-26	40	27	54	0	15	22	50
4-27	35	34	0	0	25	0	23
4-28	62	30	0	0	45	67	0
4-29	0	0	8	0	65	55	34
4-30	35	12	65	0	0	40	40
4-31	20	32	56	12	60	35	0
4-32	18	76	65	0	20	45	12
4-33	0	48	56	0	12	60	54
4-34	21	0	12	0	30	40	0
莠去津 atrazine	100	100	100	100	–	–	–
精喹禾灵 quizalofop-*p*-ethyl	–	–	–	–	100	100	100

注:" – ", 无试验数据。Note: " – ", No data.

表 6 化合物 4-1 的除草活性

Table 6 The herbicidal activity of compound **4-1**

杂草 Weeds	回归线方程(*y* =) Regression equation	相关系数 *r*	ED_{50}/(g/hm^2)
苘麻 *A. theophrasti*	1. 351 5 + 1. 747 2*x*	0. 999 0	122. 51
反枝苋 *A. retroflexus*	2. 502 8 + 1. 673 2*x*	0. 989 1	< 31. 08
藜 *C. album*	0. 511 3 + 2. 604 0*x*	0. 987 6	130. 76
狗尾草 *S. viridis*	0. 924 8 + 1. 939 0*x*	0. 953 9	126. 39
马唐 *D. sanguinalis*	5. 548 0 + 5. 334 8*x*	0. 960 7	94. 89

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