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Novel phenoxyacetic herbicides synthesized from longifolene-derived primary amine for sustainable weed management

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Because of low water solubility, herbicides containing a phenoxy acid group, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA), are applied with an amine, like dimethylamine (DMA) and isopropylamine (IPA), to form ammonium salts. However, the use of amine poses substantial health and environmental risks during manufacturing and utilization. The development of non-toxic high-performance herbicidal formulations using natural compounds is therefore highly desired but remains limited. In this work, three longifolene-derived ammonium phenoxyacetates and one glyphosate were synthesized and characterized. Their herbicidal activities were evaluated against *Lolium multiflorum Lam.* and *Brassica campestris*. The results showed that almost all target compounds exhibited higher herbicidal activity than DMA or IPA formulations prepared by their corresponding commercial herbicides. Particularly, compounds **6b** and **6c** containing the Cl atom tended to be the most active candidates, especially with notable half maximal inhibitory concentrations (IC_{50}) values of around 0.0002 mmol L^{-1} against the root and shoot growth of *Brassica campestris*, which both showed complete inhibition for *Lolium multiflorum Lam.* root growth and *Brassica campestris* shoot growth at concentrations of 0.039 and 0.156 mmol L^{-1}, respectively. In addition, compound **6c** showed a good broad-spectrum herbicidal effect on the root growth of 6 different weeds, especially on rice, with an IC_{50} of 0.000085 mmol L^{-1}. It is suggested that compounds **6b** and **6c** could be considered as promising botanical herbicides for sustainable weed management.

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Introduction

Herbicides, known as weed killers, have long provided effective solutions in agricultural practices.[1] Despite their benefits for world food production, there are several downsides. Concerns about environmental and health issues have amplified because of the presence of supplemental chemicals, which are added to herbicide formulations to modify the herbicide's properties.[2] Particularly, amines, including dimethylamine (DMA) and isopropylamine (IPA), are frequently applied in salt formulations of well-known phenoxyacetic acid herbicides [*i.e.*, phenoxyacetic acid (PA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA)] to increase herbicide solubility.[2,3] However, amines tend to have higher vapor pressures than the corresponding herbicides, could potentially volatilize from herbicide-amine salts and enter atmosphere, where they are a hazard to the social environment and living organism.[4–6] Besides, volatilized amines may additionally promote the loss of active ingredient of herbicide, which would result in heighted off-target drift damage and other serious problems.[7–10] Given the defects of the currently used commercial preparations, it is urgent to develop novel efficient, eco-friendly and low-toxicity herbicide substitutes for sustainable weed management.

As an alternative, botanical herbicides, mainly extracted or derived from plants, are gaining attention. Natural products, especially plant metabolites, have been favourable in botanical herbicide preparation owing to their unique chemical structures and diverse biological properties.[11,12] Longifolene, a naturally occurring tricyclic sesquiterpene, is the primary component of heavy turpentine.[13] As the byproduct in the production of rosin and turpentine from pine oleoresin, the sustainable biomass resource longifolene has the advantage of good bioactivities,[14,15] is reported to be used as a versatile raw material for extensive applications in many fields,[15–23] but there are few studies on the exploration of longifolene derivatives for agricultural purposes. Notably, in our previous study, ω-aminomethyl longifolene (compound **5**) with a primary amine

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group and a series of longifolene-derived primary amine carboxylates were synthesized *via* derivation of volatile longifolene, and some of them displayed significant herbicidal activity against *Lolium multiflorum Lam.* and *Brassica campestris* even at low doses.[22,23] It is worth mentioning that the half maximal inhibitory concentration (IC_{50}) values of the most active compound against the root and shoot growth of *Lolium multiflorum Lam.* and *Brassica campestris* were around 0.010 and 0.023 mmol L^{-1}.[23]

In a continuous study on the high-value-added exploration of longifolene in sustainable agriculture, three longifolene-derived phenoxyacetates and one glyphosate were synthesized from compound **5** and four globally commercial herbicides, namely PA, 2,4-D, MCPA and glyphosate. The use of compound **5** instead of hazardous amines is expected to reduce the harm caused by amine volatilization, and improve the herbicidal performance compared to commercially used herbicidal formulations or to achieve the same effects at a lower dosage. In addition to the synthesis and structural analysis, the herbicidal activity of target compounds against *Lolium multiflorum Lam.* and *Brassica campestris* were evaluated. Besides, the herbicidal spectrum experiment was also tested and described. Overall, this work is likely to facilitate the development of novel high-efficacy natural-based herbicides and expand the utilization of longifolene-derived compounds in agricultural fields.

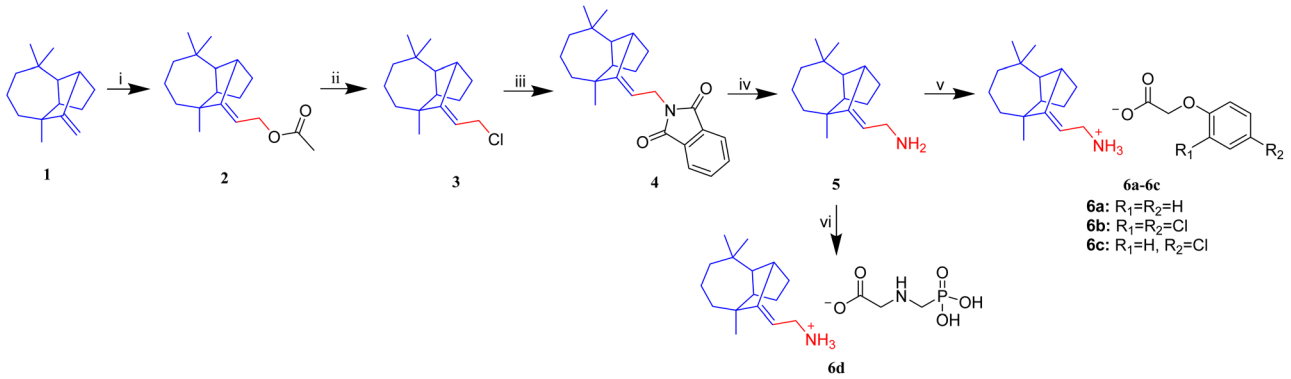
Results and discussion

Synthesis and characterization

As shown in Scheme 1, target compounds **6a–6d** can be prepared *via* a five-step synthetic route using longifolene (compound **1**) as the starting material. Intermediates **2** and **3** were synthesized according to the methods that previously reported.[24,25] Compound **3** with yield of 94.2% was obtained through Prins and halogenation reaction from compound **1**.[25] In the presence of potassium phthalimide, compound **3** reacted with dimethyl formamide (DMF) at 110 °C for 2 h, and compound **4** was produced with yield of 82.0%.[22,23] Subsequently, compound **5**, yielding 94.1%, was synthesized by modification of the route based on Gabriel synthesis.[26] Finally, compounds **6a–6d** were prepared from the reaction between compound **5** and the corresponding phenoxyacetic acids (PA, 2,4-D and MCPA) and glyphosate, respectively. These compounds were confirmed by FTIR, ^{1}H and ^{13}C NMR spectroscopy, and HRMS. In the FTIR spectra, the peak at 3100–3000 cm^{-1} was characteristic of the C–H stretching vibration band in the aromatic ring. The peaks in the ranges of 2958–2866 cm^{-1}, 1685–1635 cm^{-1}, 1593–1490 cm^{-1} and 1390–1300 cm^{-1} represented the stretching vibration band of C–H alkane groups, the stretching vibration band of the C=O bonds of the carboxyl group, the stretching vibration band of the C=C bonds of an aromatic ring, and the stretching vibration band of C–N bonds, respectively (Fig. S1–S4, SI). In the ^{1}H NMR spectra, three singlets at δ 0.92–0.83 ppm revealed the presence of three isolated methyl groups in ω-aminomethyl longifolene moiety. The triple at δ 5.04–4.86 ppm was assigned to the signal of H-13 and the singlet at δ 4.67–4.39 ppm belonged to the hydrogen proton of the isolated methene hydrogen proton in phenoxyacetate moiety. The chemical shifts at 7.35–6.81 ppm were attributed to hydrogen protons on the aromatic ring (Fig. S5–S8). In the ^{13}C NMR spectra, peaks ranging from δ 165.32–106.97 ppm were assigned to the phenyl and carbon–carbon double bond. The peak with δ 175.14–173.94 ppm was attributed to carbonyl, and peaks with δ 68.66–16.34 ppm were assigned to the *p*-menthane (Fig. S9–S12). The total number of hydrogen and carbon atoms is consistent with that of the corresponding compounds, and it was further confirmed by HRMS that compounds **6a–6d** are longifolene-derived ammonium phenoxyacetates and glyphosate (Fig. S13–S16).

Herbicidal activities

In this work, target compounds **6a–6d** were evaluated for herbicidal activity against *Lolium multiflorum Lam.* and *Brassica campestris*. Several commercial herbicides, including PA, 2,4-D, MCPA and glyphosate, were chosen as positive controls. The inhibition rates of those tested compounds were summarized in Tables 1–4, and the toxicity regression equations and IC_{50} values were shown in Tables 5 and 6. All the synthesized compounds **6a–6d** exhibited higher or comparable herbicidal activity than their corresponding DMA or IPA salts. The



Scheme 1 Synthetic route of target compounds **6a–6d** (i) CH_3COOH, $(HCHO)_n$, reflux, 24 h; (ii) CH_3COCl, reflux, 1 h; (iii) potassium phthalimide, DMF, 2h; (iv) $N_2H_4 \cdot H_2O$, NaOH, reflux, 6 h; (v) absolute alcohol, 80 °C, 1.5 h; (vi) glyphosate, deionized water, RT, 30 min.

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Table 1 Inhibition rates of compounds on the root growth of *Lolium multiflorum* Lam

	Concentrations (mmol L^{-1})									
Compd	1.25[a]	0.625[a]	0.313[a]	0.156[a]	0.078[a]	0.039[a]	0.020[a]	0.010[a]	0.005[a]	0.002[a]
5	100[b]	100	100	94.1	70.4	44.0	31.8	23.3	12.9	8.24
6a	100	100	100	95.1	93.4	36.2	9.1	[c]	[c]	[c]
6b	100	100	100	100	100	100	90.0	81.1	39.5	12.7
6c	100	100	100	100	100	100	96.2	89.1	70.1	54.4
6d	100	100	100	98.0	94.7	64.6	11.3	−17.7	−27.9	−24.3
DMA salt of PA	[c]	46.7	16.2	13.8	4.1	1.8	0.1	−1.1	−5.3	−5.1
DMA salt of 2,4-D	[c]	100	100	98.2	97.2	83.9	70.5	36.1	6.0	2.1
DMA salt of MCPA	[c]	99.9	99.8	99.3	97.6	98.4	96.0	90.8	77.5	87.8
GLYP-IPAM salt	[c]	88.2	87.9	84.5	72.4	60.9	51.9	50.7	43.9	27.3

[a] The concentration of different longifolene-derived compounds and four ammonium salts solutions (mmol L^{-1}). [b] The inhibition rate (%). [c] The data at this concentration were not determined.

Table 2 Inhibition rates of compounds on the shoot growth of *Lolium multiflorum* Lam

	Concentrations (mmol L^{-1})									
Compd	1.25[a]	0.625[a]	0.313[a]	0.156[a]	0.078[a]	0.039[a]	0.020[a]	0.010[a]	0.005[a]	0.002[a]
5	100[b]	89.8	78.8	61.7	47.7	37.4	28.0	25.6	10.6	1.87
6a	100	100	98.2	59.6	45.0	21.9	0	[c]	[c]	[c]
6b	100	100	100	79.7	64.3	58.1	44.2	33.2	−0.66	−15.8
6c	100	100	100	100	78.6	62.5	53.3	46.3	29.8	24.9
6d	100	100	100	52.8	31.5	30.9	−12.2	−8.68	−12.7	−16.9
DMA salt of PA	[c]	16.6	12.4	10.0	1.0	1.0	−4.3	−9.3	−13.1	−10.5
DMA salt of 2,4-D	[c]	95.9	91.5	70.0	68.7	53.8	49.4	35.7	13.6	10.8
DMA salt of MCPA	[c]	63.1	63.0	61.5	57.9	57.3	56.6	54.1	48.7	35.8
GLYP-IPAM salt	[c]	58.0	55.2	42.7	42.3	35.1	26.0	22.0	18.6	14.0

[a] The concentration of different longifolene-derived compounds and four ammonium salts solutions (mmol L^{-1}). [b] The inhibition rate (%). [c] The data at this concentration were not determined.

ammonium salt formed by glyphosate and IPA was named GLYP-IPAM salt. Moreover, those tested compounds possessed remarkable inhibition rates for the root growth but low inhibition rates for the shoot growth of *Lolium multiflorum Lam.* and *Brassica campestris*. It can also be observed that the inhibition rates of compounds **5** and **6a–6d** were increased with the increase of applications in the range of 0.002 to 1.25 mmol L^{-1} under certain circumstances. Furthermore, it was found that compounds **6b** and **6c** containing the Cl atom displayed the strongest herbicidal activity against the root and shoot growth of *Lolium multiflorum Lam.* and *Brassica campestris* within the tested concentration range. Impressively, compound **6b** had the most potent inhibition efficacy for *Brassica campestris* root, which maintained an excellent level of effectiveness at

Table 3 Inhibition rates of compounds on the root growth of *Brassica campestris*

	Concentrations (mmol L^{-1})									
Compd	1.25[a]	0.625[a]	0.313[a]	0.156[a]	0.078[a]	0.039[a]	0.020[a]	0.010[a]	0.005[a]	0.002[a]
5	100[b]	100	100	94.3	60.1	40.4	31.4	22.9	13.6	0.16
6a	100	100	100	100	79.1	31.8	−26.3	[c]	[c]	[c]
6b	100	100	100	100	100	100	100	99.0	97.6	96.3
6c	100	100	100	100	100	98.6	96.0	93.4	90.0	88.0
6d	100	100	100	96.3	90.4	61.6	36.1	11.7	−1.17	0.74
DMA salt of PA	[c]	89.0	82.2	67.6	41.7	40.3	27.1	18.5	4.5	−5.5
DMA salt of 2,4-D	[c]	92.8	90	88.1	86.3	85.9	83.8	82.8	82.1	81.8
DMA salt of MCPA	[c]	100	100	100	100	100	100	100	100	100
GLYP-IPAM salt	[c]	79.5	71.2	64.5	63.6	48.2	42.5	24.1	15.7	6.63

[a] The concentration of different longifolene-derived compounds and four ammonium salts solutions (mmol L^{-1}). [b] The inhibition rate (%). [c] The data at this concentration were not determined.

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Table 4 Inhibition rates of compounds on the shoot growth of *Brassica campestris*

	Concentrations (mmol L^{-1})									
Compd	1.25[a]	0.625[a]	0.313[a]	0.156[a]	0.078[a]	0.039[a]	0.020[a]	0.010[a]	0.005[a]	0.002[a]
5	100[b]	87.7	76.7	57.5	40.8	35.0	28.2	21.4	19.4	5.44
6a	100	96.5	71.7	54.6	31.2	10.4	9.1	[c]	[c]	[c]
6b	100	100	100	100	96.1	95.1	92.1	91.2	90.0	88.0
6c	100	100	100	100	98.4	97.2	94.3	91.1	87.0	82.6
6d	100	100	100	63.1	49.1	−1.22	−7.30	−2.74	−0.84	−3.59
DMA salt of PA	[c]	63.9	50.2	32.9	12.3	12.9	7.4	5.1	−4.5	3.0
DMA salt of 2,4-D	[c]	86.8	84.3	82.2	80.1	78.5	76.8	76.3	76.1	71.6
DMA salt of MCPA	[c]	93.8	92	87.5	86.6	84.8	82.0	81.1	79.0	77.1
GLYP-IPAM salt	[c]	57.9	35.7	32.2	23.3	23.0	22.5	15.6	12.4	8.2

[a] The concentration of different longifolene-derived compounds and four ammonium salts solutions (mmol L^{-1}). [b] The inhibition rate (%). [c] The data at this concentration were not determined.

Table 5 Toxicity regression equations and IC_{50} of compounds against *Lolium multiflorum* Lam.

	Root		Shoot	
Compd	Toxicity regression equation	IC_{50} (mmol L^{-1})	Toxicity regression equation	IC_{50} (mmol L^{-1})
5	$Y = 2.572 + 1.675x$ $R^2 = 0.929$	0.0291	$Y = 1.553 + 1.274x$ $R^2 = 0.962$	0.0604
6a	$Y = 5.291 + 3.894x$ $R^2 = 0.919$	0.0438	$Y = 3.130 + 3.204x$ $R^2 = 0.887$	0.105
6b	$Y = 5.084 + 2.281x$ $R^2 = 0.975$	0.0059	$Y = 2.313 + 1.467x$ $R^2 = 0.984$	0.0265
6c	$Y = 5.267 + 2.005x$ $R^2 = 0.991$	0.0024	$Y = 2.446 + 1.288x$ $R^2 = 0.977$	0.0126
6d	$Y = 6.104 + 4.173x$ $R^2 = 0.947$	0.034	$Y = 2.534 + 2.458x$ $R^2 = 0.772$	0.093
DMA salt of PA	$Y = 0.152 + 1.704x$ $R^2 = 0.96$	0.814	$Y = -0.641 + 2.389x$ $R^2 = 0.929$	3.157
DMA salt of 2,4-D	$Y = 4.617 + 2.508x$ $R^2 = 0.976$	0.014	$Y = 1.73 + 1.113x$ $R^2 = 0.028$	0.969
DMA salt of MCPA	$Y = 3.928 + 1.336x$ $R^2 = 0.908$	0.001	$Y = 0.654 + 0.452x$ $R^2 = 0.662$	0.036
GLYP-IPAM salt	$Y = 1.455 + 0.755x$ $R^2 = 0.966$	0.012	$Y = 0.388 + 0.516x$ $R^2 = 0.962$	0.177

a concentration as low as 0.002 mmol L^{-1}, and displayed 100% inhibition rate to the root growth of *Brassica campestris* at the dosage of 0.020 mmol L^{-1}. When treated at a higher concentration (0.078 mmol L^{-1}), compound **6c** also presented a 100% inhibition rate to the root growth of *Brassica campestris*.

For *Lolium multiflorum Lam.*, the herbicidal activity of compounds **6b** and **6c** were higher than that of compounds **5**, **6a** and **6d**. Their inhibition rates for root growth were exceeded 90% at the concentration of 0.02 mmol L^{-1} and reached 100% at 0.039 mmol L^{-1}. The inhibition rate of compound **6c** on shoot growth were 100% when treated at 0.156 mmol L^{-1}. It is worth noting that almost all the synthesized compounds completely inhibited *Lolium multiflorum Lam.* root and shoot growth at 0.313 mmol L^{-1} (Fig. S17 and S19). On the other hand, the order of the herbicidal activity against the root growth of *Brassica campestris* was **6b** > **6c** > **6a** > **6d** > **5**, while the order of the herbicidal activity against the shoot growth was **6c** ≥ **6b** > **6d** > **6a** > **5**. Compound **6c** exhibited a slightly elevated control over *Brassica campestris* shoot growth in comparison to compound **6b** when applied at the concentration ranging from 0.02 to 0.078 mmol L^{-1}. However, the inhibitory effects of compounds **6b** and **6c** against the shoot growth of *Brassica campestris* were the same with 100% inhibition at the concentration of 0.156 mmol L^{-1} (Fig. S18 and S20). Although compound **6c** demonstrated excellent inhibition rates for root growth, its older DMA salt formulation exhibited superior herbicidal performance, which showed complete inhibition even at 0.002 mmol L^{-1}. The inhibition rate of compound **6a** for *Brassica campestris* root growth was higher than that for shoot growth, at the concentration of 0.156 mmol L^{-1}, the inhibition rates against shoot growth were 54.6%, but against root growth reached 100%. Additionally, compound **6d** showed 100% of control efficacy both on *Brassica campestris* root and shoot growth at the dosage of 0.313 mmol L^{-1} (Fig. S21–S22).

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Table 6 Toxicity regression equations and IC_{50} of compounds against *Brassica campestris*

	Root		Shoot	
Compd	Toxicity regression equation	IC_{50} (mmol L^{-1})	Toxicity regression equation	IC_{50} (mmol L^{-1})
5	$Y = 2.621 + 1.790x$ $R^2 = 0.886$	0.0340	$Y = 1.391 + 1.156x$ $R^2 = 0.951$	0.0630
6a	$Y = 6.040 + 4.702x$ $R^2 = 0.982$	0.0520	$Y = 1.903 + 2.185x$ $R^2 = 0.941$	0.1350
6b	$Y = 5.552 + 1.486x$ $R^2 = 0.966$	0.0002	$Y = 2.847 + 0.711x$ $R^2 = 0.898$	0.0001
6c	$Y = 3.541 + 0.953x$ $R^2 = 0.947$	0.0002	$Y = 0.3210 + 0.896x$ $R^2 = 0.993$	0.0003
6d	$Y = 4.048 + 2.605x$ $R^2 = 0.991$	0.028	$Y = 3.291 + 3.168x$ $R^2 = 1.000$	0.092
DMA salt of PA	$Y = 1.457 + 1.258x$ $R^2 = 0.972$	0.069	$Y = 0.458 + 1.085x$ $R^2 = 0.917$	0.379
DMA salt of 2,4-D	$Y = 0.916 + 0.169x$ $R^2 = 0.745$	0.000034	$Y = 0.532 + 0.197x$ $R^2 = 0.685$	0.002
DMA salt of MCPA	$Y = 6.355 + 1.509x$ $R^2 = 0.873$	0.000061	$Y = 1.139 + 0.099x$ $R^2 = 0.923$	0.000147
GLYP-IPAM salt	$Y = 1.226 + 0.96x$ $R^2 = 0.967$	0.053	$Y = 0.107 + 0.589x$ $R^2 = 0.941$	0.657

As shown in Table 5, the IC_{50} values of compounds **6a–6d** against *Lolium multiflorum Lam.* root and shoot growth were 0.0024–0.0438 and 0.0126–0.1050 mmol L^{-1}, respectively. Among them, compounds **6b** and **6c** possessed much lower IC_{50} values than that of compound **5** (IC_{50} values of root and shoot growth were 0.0291 and 0.0604 mmol L^{-1}, respectively). It seemed that the IC_{50} values of compounds **6a–6c** against *Lolium multiflorum Lam.* root and shoot growth were lower than that of their corresponding DMA salts. The IC_{50} value of compound **6d** against *Lolium multiflorum Lam.* root growth was lower than that of GLYP-IPAM salt, but higher than GLYP-IPAM salt against *Lolium multiflorum Lam.* shoot growth. According to Fig. 1, the herbicidal activity of compound **6a** against root growth of *Lolium multiflorum Lam.* was more than 18 times higher than that of DMA salt of PA, and the herbicidal activity of compound **6b** was 137.3% higher than that of DMA salt of 2,4-D against *Lolium multiflorum Lam.* root growth. Similarly, compounds **6a** and **6b** showed 2906.7% and 3556.6% higher herbicidal activity against *Lolium multiflorum Lam.* shoot growth than their corresponding DMA salts, respectively. Moreover, compounds **6c** and **6d** exhibited 185.7% and 90.3% higher herbicidal activity against *Lolium multiflorum Lam.* shoot growth than DMA salt of MCPA and GLYP-IPAM salt, respectively.

From Table 6, the IC_{50} values of compounds **6a–6d** against *Brassica campestris* root and shoot growth were 0.0002–0.052 mmol L^{-1} and 0.0001–0.135 mmol L^{-1}, respectively. In particular, compounds **6b** and **6c** with the lowest IC_{50} values (around 0.0002 mmol L^{-1}) were more favourable to herbicidal activity than compounds **5**, **5a** and **5d**. It is important to note that compound **6b** displayed 200 times higher herbicidal activity against *Brassica campestris* shoot growth than DMA salt of 2,4-D. Moreover, compounds **6a** and **6d** both had lower IC_{50} values than their DMA/IPA salt. It can be seen from Fig. 2 that compounds **6a** and **6d** presented 180.7% and 614.1% higher

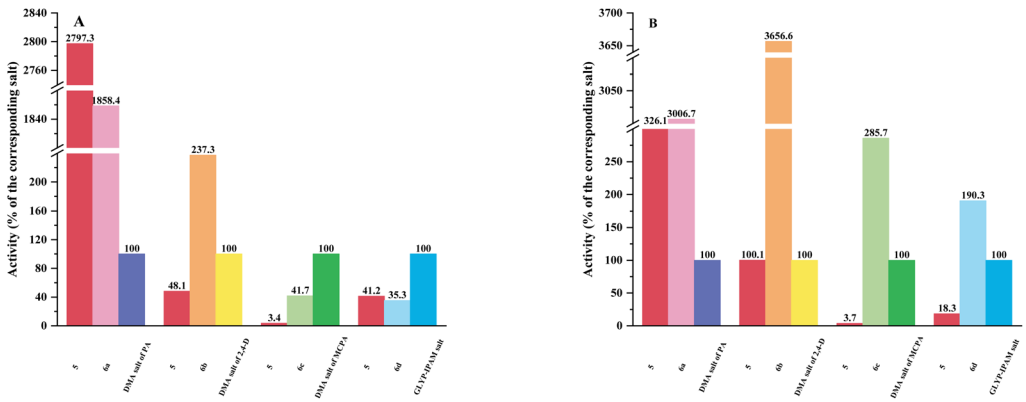

Fig. 1 Herbicidal effects of compounds against the root growth (A) and shoot growth (B) of *Lolium multiflorum Lam.* compared to that of their corresponding DMA/IPA salts.

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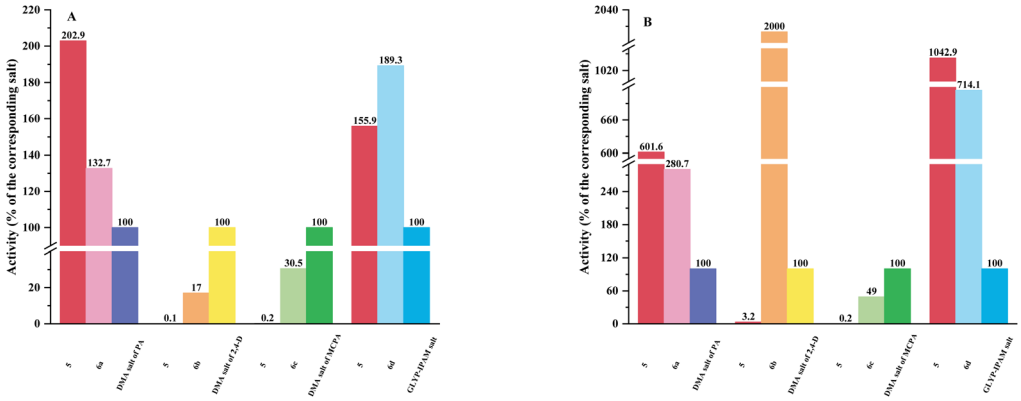

Fig. 2 Herbicidal effects of compounds against the root growth (A) and shoot growth (B) of *Brassica campestris* compared to that of their corresponding DMA/IPA salts.

Table 7 Inhibition rates of compound **6c** against different plants

Concentrations (mmol L^{-1})	*Setaria viridis*		*Eleusine indica*		Rice		*Portulaca oleracea*		*Medicago sativa* L.		Clover	
	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot
0.0001	45.2	−9.07	39.6	3.98	72.4	11.8	38.4	−7.35	19.8	18.5	47.1	7.53
0.0006	58.1	8.27	43.7	21.1	84.8	12.5	41.6	−5.39	43.8	24.1	67.3	10.3
0.001	74.2	9.33	63.5	21.9	94.1	15.1	67.2	7.35	58.3	37.7	76.9	33.6
0.002	77.4	24.0	62.9	20.3	95.9	13.2	84.8	27.5	66.7	63.5	79.8	57.5
0.010	83.9	50.4	85.3	25.9	100	−1.32	95.6	26.9	63.5	81.5	85.7	81.5
0.039	100	71.7	91.4	43.4	100	32.2	96.8	77.0	76.0	84.8	95.2	95.9

herbicidal activity against *Brassica campestris* shoot growth than their corresponding salts, and their herbicidal activities against *Brassica campestris* root growth were 32.7% and 89.3% higher than that of DMA salt of PA and GLYP-IPAM salt, respectively. For compounds **6b** and **6c** containing one or two chlorine atoms, despite they displayed higher inhibition rates and lower IC_{50} values than their corresponding DMA salts for the root and shoot growth of *Brassica campestris* in most cases, only compound **6b** had a relatively lower IC_{50} value against *Brassica campestris* shoot growth than DMA salt of 2,4-D.

Herbicidal spectrum of compound 6c

Based on the results, the IC_{50} values of compound **6c** against *Lolium multiflorum Lam.* and *Brassica campestris* were almost the lowest among the prepared compounds, compound **6c** was further examined for its inhibitory effects on six different types

Table 8 Toxicity regression equations and IC_{50} of compound **6c** against different plants

Plants	Root		Shoot	
	Toxicity regression equation	IC_{50} (mmol L^{-1})	Toxicity regression equation	IC_{50} (mmol L^{-1})
Setaria viridis	$Y = 2.498 + 0.649x$ $R^2 = 0.947$	0.000142	$Y = 2.304 + 1.179x$ $R^2 = 0.979$	0.0111
Eleusine indica	$Y = 2.486 + 0.774x$ $R^2 = 0.933$	0.000612	$Y = 0.510 + 0.493x$ $R^2 = 0.897$	0.0922
Rice	$Y = 5.448 + 1.338x$ $R^2 = 0.882$	0.000085	$Y = -0.40 + 0.343x$ $R^2 = 0.846$	1.31
Portulaca oleracea	$Y = 2.935 + 0.817x$ $R^2 = 0.894$	0.000257	$Y = 2.351 + 1.146x$ $R^2 = 0.910$	0.00887
Medicago sativa L.	$Y = 1.253 + 0.389x$ $R^2 = 0.784$	0.000602	$Y = 2.531 + 0.929x$ $R^2 = 0.931$	0.00188
Clover	$Y = 2.912 + 0.805x$ $R^2 = 0.921$	0.000241	$Y = 3.633 + 1.376x$ $R^2 = 0.944$	0.00229

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of weeds (Table 7). It is shown that compound **6c** had different inhibitory activities in the concentration range of 0.0001–0.039 mmol L^{-1}. Compound **6c** was more sensitive on the root growth of those weeds than that on the shoot growth, and its inhibition rates were also related to the applied concentration. At the concentration of 0.010 mmol L^{-1}, compound **6c** displayed over 80% inhibition against the root growth of *Setaria viridis*, *Eleusine indica*, rice, *Portulaca oleracea* and clover, whereas, compound **6c** only exhibited less than 30% inhibition against the shoot growth of *Eleusine indica*, rice and *Portulaca oleracea* at the same dosage. When the concentration was 0.039 mmol L^{-1}, the inhibition rates of compound **6c** on the root growth of two monocotyledonous weeds (*Setaria viridis* and rice) were 100%, while the inhibition rate on the root growth of *Eleusine indica* was 91.4%. In terms of dicotyledonous weeds, compound **6c** displayed > 95% inhibition against *Portulaca oleracea* root growth and clover root and shoot growth when treated at 0.039 mmol L^{-1}, whereas compound **6c** only displayed < 85% inhibition against *Medicago sativa* L. root and shoot growth and *Portulaca oleracea* shoot growth at the same concentration. Additionally, compound **6c** had much lower IC_{50} values against the root growth of the tested weeds than that against the shoot growth, as the IC_{50} values of root and shoot growth were 0.000085–0.000612 and 0.00188–1.31 mmol L^{-1}, respectively (Table 8). In general, compound **6c** showed good broad-spectrum weed control against the weeds tested, and the control effect on the root growth was better than that on the shoot growth, especially for monocotyledonous weeds.

Conclusions

In summary, a library of novel ammonium phenoxyacetates and glyphosate based on longifolene-derived primary amine were synthesized and characterized. Herbicidal activity evaluation showed that the majority of the synthesized compounds performed better than their corresponding herbicide-amine salts. Compounds **6b** and **6c** with the Cl atom displayed the most potent herbicidal efficacy for *Lolium multiflorum Lam.* and *Brassica campestris*, *Lolium multiflorum Lam.* root growth and *Brassica campestris* shoot growth were both completely inhibited when their treated concentrations were 0.039 and 0.156 mmol L^{-1}. Moreover, the root growth of *Brassica campestris* was completely inhibited by compounds **6b** and **6c** at the concentrations of 0.02 and 0.078 mmol L^{-1}, respectively. Furthermore, compound **6c** was found to have a broad spectrum of weed control and displayed a good herbicidal effect on the root growth of the experimental weeds at 0.039 mmol L^{-1}. Those findings indicated that compounds **6b** and **6c** would have great potential to serve as high-performance botanical herbicide candidates used at low doses.

Experimental section

Material

Heavy turpentine was obtained commercially from Guangxi Wusong Pine Chemicals Group Co., Ltd (Guangxi, China). Longifolene (compound **1**) with a boiling point of 252–254 °C was synthesized from heavy turpentine based on a previously published method.[27] Compounds **2** and **3** were prepared following the procedure reported in our previous work.[24,25] Compound **3** was obtained by the Prins and halogenation reaction from compound **1**,[24] and compound **4** was prepared by using potassium phthalimide.[22,23] PA, 2,4-D, MCPA, glyphosate, acetonitrile and DMF were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Absolute alcohol, sodium hydroxide (NaOH), Tween 80, deuterated trichloromethane ($CDCl_3$), deuterated methanol (CD_3OD) and ethyl acetate were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). *Lolium multiflorum Lam.* and *Brassica campestris* were purchased from Barenbrug International Co., Ltd (Tianjin, China), and Shenzhen Aoxin Libao Industrial Co., Ltd (Shenzhen, China), respectively. Different formulations of DMA salts and GLYP-IPAM salt were prepared through the neutralization reaction in our labs according to the procedure described in patents.[28,29]

Synthesis of compound 5

Compound **5** was synthesized in accordance with the procedure in our previous study.[22,23] To a mixture of compound **4** (2.181 g, 6 mmol) and 80% $N_2H_4 \cdot H_2O$ (8.635 g, 138 mmol), 5 g of 10% aqueous NaOH solution was added. Then, the reaction mixture was refluxed for 6 h at 120 °C. After cooling, the mixture was extracted with petroleum ether (3 × 10 mL). The combined organic phase was washed with distilled water (3 × 10 mL) and dried over anhydrous Na_2SO_4 and then evaporated the solvent in a vacuum to gain compound **5** as a pale-yellow oily liquid with yield of 94.1%. The boiling point of compound **5** was 288–290 °C.

Synthesis of compounds 6a–6c

The preparation of compounds **6b** and **6c** followed the typical procedure described below for the preparation of compound **6a**. PA (0.76 g, 5 mmol) was added to a three-necked flask with absolute alcohol (15 mL), respectively. The mixture was stirred for 15 min at room temperature, and a mixture of compound **5** (1.17 g, 5 mmol) in absolute alcohol (8 mL) was added dropwise. Then, the reaction mixture was heated to 80 °C and stirred for 1.5 h. After cooling to room temperature, the mixture was evaporated to remove the volatile compounds. The crude produce was washed with absolute alcohol and ethyl acetate (5 : 1, v/v) to obtain compound **6a**.

(*E*)-2-(4,8,8-trimethyldecahydro-1,4-methanoazulen-9-ylidene)ethan-1-aminium 2-phenoxyacetate (**6a**). Yield: 81.7%; white powder; melting point (mp), 133.1–134.1 °C. FT-IR (KBr) ν (cm^{-1}): 3115.16, 2958.80, 2929.87, 1685.79, 1639.49, 1597.06, 1571.99, 1544.98, 1496.76, 1473.62, 1456.26, 1415.75, 1375.25, 1338.60, 1288.45, 1236.37, 1174.65, 1084.00, 1055.06, 937.40, 837.11, 748.38, 707.88, 688.59. ^{1}H NMR (400 MHz, CD_3OD) δ (ppm), 7.35–7.16 (m, 2H), 7.02–6.82 (m, 3H), 5.04 (t, ^{1}H, $J = 7.1$ Hz), 4.39 (s, 2H), 3.67–3.49 (m, 2H), 2.97 (d, ^{1}H, $J = 4.9$ Hz), 2.17 (d, ^{1}H, $J = 3.5$ Hz), 1.81 (tdd, ^{1}H, $J = 12.0$, 5.0, 3.3 Hz), 1.75–1.59 (m, 3H), 1.58–1.41 (m, 4H), 1.22–1.07 (m, 2H), 1.04 (s, 3H), 1.00 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm), 175.01, 164.52, 158.55, 129.51, 120.89, 114.69, 107.49, 67.64, 62.35,

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44.77, 44.43, 43.23, 42.32, 38.33, 36.49, 33.48, 30.94, 30.19, 30.04, 28.66, 25.45, 20.86. HRMS (ESI) *m/z* $[M–C_8H_7O_3–NH_3]^+$ calculated for $C_{16}H_{25}$ 217.1956, found 217.1960; $[M-C_{16}H_{28}N]^-$ calculated for $C_8H_7O_3$ 151.0395, found 151.0397.

(*E*)-2-(4,8,8-trimethyldecahydro-1,4-methanoazulen-9-ylidene)ethan-1-aminium 2-(2,4-dichlorophenoxy)acetate (**6b**). Yield: 90.6%; white powder; mp 145.9–146.7 °C. FT-IR (KBr) ν (cm^{-1}): 3113.11, 3051.39, 2947.23, 2866.22, 1635.64, 1593.20, 1529.55, 1477.47, 1402.25, 1284.59, 1263.38, 1232.51, 1105.21, 1068.56, 1039.63, 908.47, 869.90, 835.18, 804.32, 719.45, 646.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm), 7.33 (d, ^{1}H, $J = 2.5$ Hz), 7.13 (dd, ^{1}H, $J = 8.8$, 2.5 Hz), 6.81 (d, ^{1}H, $J = 8.9$ Hz), 4.89 (t, ^{1}H, $J = 7.0$ Hz), 4.42 (s, 2H), 3.41 (dd, 2H, $J = 6.9$, 3.1 Hz), 2.73 (d, ^{1}H, $J = 4.6$ Hz), 2.05 (d, ^{1}H, $J = 3.1$ Hz), 1.66 (s, ^{1}H), 1.59–1.47 (m, 3H), 1.36 (ddd, 5H, $J = 24.5$, 17.5, 10.9 Hz), 1.00 (ddd, 2H, $J = 17.2$, 9.8, 5.1 Hz), 0.92 (s, 3H), 0.88 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm), 173.94, 165.29, 153.07, 129.97, 127.72, 125.97, 123.17, 114.63, 107.01, 68.66, 62.34, 44.70, 44.46, 43.25, 42.35, 38.48, 36.50, 33.46, 30.89, 30.15, 30.00, 28.72, 25.41, 20.85. HRMS (ESI) *m/z* $[M–C_8H_5O_3Cl_2–NH_3]^+$ calculated for $C_{16}H_{25}$ 217.1956, found 217.1956; $[M–C_{16}H_{28}N]^-$ calculated for $C_8H_5O_3Cl_2$ 218.9616, found 218.9608.

(*E*)-2-(4,8,8-trimethyldecahydro-1,4-methanoazulen-9-ylidene)ethan-1-aminium 2-(4-chloro-2-methylphenoxy)acetate (**6c**). Yield: 73.4%; white powder; mp 155.8–156.5 °C. FT-IR (KBr) ν (cm^{-1}): 3057.17, 2956.88, 2924.09, 2912.51, 2879.72, 2866.22, 1635.64, 1593.20, 1560.41, 1490.98, 1456.26, 1404.18, 1371.39, 1298.09, 1257.59, 1228.66, 1190.08, 1134.14, 1060.85, 877.61, 804.32, 705.95, 646.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm), 7.08 (d, ^{1}H, $J = 2.0$ Hz), 7.04 (dd, 1H, $J = 8.6$, 2.4 Hz), 6.66 (d, ^{1}H, $J = 8.6$ Hz), 4.86 (s, ^{1}H), 4.37 (s, 2H), 3.26 (t, 2H, $J = 7.4$ Hz), 2.70 (d, ^{1}H, $J = 4.5$ Hz), 2.22 (s, 3H), 2.06 (d, ^{1}H, $J = 2.7$ Hz), 1.76–1.62 (m, ^{1}H), 1.59–1.48 (m, 3H), 1.35 (ddd, 5H, $J = 30.1$, 22.2, 8.8 Hz), 1.09–0.98 (m, 2H), 0.92 (s, 3H), 0.89 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm), 175.14, 165.32, 155.62, 130.56, 128.66, 126.41, 125.41, 112.91, 106.97, 68.34, 62.34, 44.69, 44.46, 43.25, 42.33, 38.32, 36.53, 33.47, 30.93, 30.16, 30.01, 28.71, 25.41, 20.85, 16.34. HRMS (ESI) *m/z* $[M–C_9H_8O_3Cl]^+$ calculated for $C_{16}H_{28}N$ 234.2222, found 234.2222; $[M–C_{16}H_{28}N]^-$ calculated for $C_9H_8O_3Cl$ 199.0162, found 199.0153.

Synthesis of compounds 6d

Compound **5** (0.234 g, 1 mmol) and glyphosate (0.169 g, 1 mmol) were added to 10 mL of deionized water at room temperature for 30 min to obtain a homogenous solution. After that, acetonitrile was added dropwise into the solution. When milky turbid appeared in the solution system, the precipitate was collected by centrifugation. The collected solid was then processed by vacuum drying to obtain compound **6d**.

(*E*)-2-(4,8,8-trimethyldecahydro-1,4-methanoazulen-9-ylidene)ethan-1-aminium (phosphonomethyl)glycinate (**6d**). Yield: 82.2%; white powder; mp 168.2–182.3 °C. FT-IR (KBr) ν (cm^{-1}): 3397, 3331, 2955, 2851, 1738, 1640, 1157, 1025, 907, 748. ^{1}H NMR (400 MHz, D_2O) δ (ppm), 4.98–5.02 (t, ^{1}H, H-2′, $J = 8.0$ Hz), 3.69 (s, 2H, H-2″), 3.57–3.65 (m, 2H, H-1′), 3.15–3.18 (d, $J = 12.0$ Hz, 2H, H-4″), 2.92–2.93 (d, $J = 4.0$ Hz, ^{1}H, N**H**), 2.12–2.13 (d, ^{1}H, H-1), 1.69–1.73 (m, ^{1}H, H-3eq), 1.57–1.63 (m, 3H, H-3ax, H-6eq, H-2eq), 1.49–1.61 (m, 2H, H-6ax, H-2ax), 1.31–1.44 (m, 3H, H-3a, H-5eq, H-7eq), 1.09–1.14 (m, ^{1}H, H-7ax), 0.98–1.04 (m, 2H, H-5ax, H-8a), 0.93 (s, 3H, 8-C**H**$_3$), 0.90 (s, 3H, 8-C**H**$_3$), 0.82 (s, 3H, 4-C**H**$_3$). ^{13}C NMR (100 MHz, D_2O) δ (ppm), 170.81, 167.89, 105.24, 61.93, 50.43, 44.59, 44.34, 44.18, 43.22, 42.92, 42.17, 38.46, 36.19, 32.81, 30.14, 29.37, 28.41, 24.89, 23.11. HRMS (SI) *m/z* $[M–NH_3]^+$ calculated for $C_{16}H_{25}$ 217.1956, found 217.1958; $[M–C_{16}H_{28}N]^-$ calculated for $C_3H_7NO_5P^-$ 168.0067, found 165.0059.

Characterization

Structural elucidation of all the synthesized compounds were achieved by proton and carbon NMR spectroscopy. Proton (^{1}H) and carbon (^{13}C) NMR spectrum of the products were recorded on a Bruker Ascend™ 400 MHz spectrometer (Bruker Co., Ltd, Fällanden, Switzerland) with $CDCl_3$ or CD_3OD as the solvent and tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were recorded using a Magna-IR 550 (II) Fourier transform infrared spectrometer (Nicolet Co., Ltd, USA) with the use of potassium bromide pellets. All the spectra were captured in the 400–4000 cm^{-1} region, at a resolution of 4 and 64 scans per sample. Before analyzing each sample, the air was used as a reference. The HRMS spectral analysis was performed on an Agilent mass spectrometer (Agilent Technologies, Palo Alto, USA) under electron spray ionization. The melting point was measured by Beijing Taike point apparatus (X-4) and was uncorrected, and the boiling point was determined through a simple distillation method.

Herbicidal activity evaluation

According to the method reported in the literature, herbicidal activity was evaluated with three replicates per treatment.[30,31] *Lolium multiflorum Lam.* and *Brassica campestris* were selected to assess the preliminary herbicidal activity of compounds **6a–6d**. The target compounds (2 mmol) were dissolved respectively in 0.5 mL DMF in a 100 mL volumetric flask to create a mother solution of 20 mmol L^{-1}. These solutions were further diluted using 1% Tween-80 and distilled water to achieve the desired concentration. The same amount of distilled water including DMF and Tween-80 was served as the blank control. The seeds were steeped in 2% sodium hypochlorite solution for 5 min, washed with distilled water three times, and soaked in distilled water for 15 h. Afterwards, the treated seeds were placed in Petri dishes (9 cm in diameter) and incubated at 25 °C for 24 h. Ten seeds were chosen to each Petri dishes (9 cm in diameter) containing two pieces of filter paper and 10 mL test solution, incubated in dark for 3 days at 25 °C. The root or shoot length of each seed was measured. The results were expressed as the average of three independent experiments. The inhibition rate of the root or shoot growth of tested seeds was calculated by equation below, the root or shoot growth of tested seeds less than 1 mm would not take into consideration.

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$$P = \frac{L_0 - L}{L_0} \times 100\%$$

where P is the inhibition rate of the root or shoot growth, L_0 is the average root or shoot length of the blank control group in each test, and L is the average root or shoot length of the group treated with the test compounds.

Weed spectrum testing

Further the herbicidal activity study of the compound with the most significant herbicidal activity against *Lolium multiflorum Lam.* and *Brassica campestris* was also performed for several representative monocotyledonous and dicotyledonous weeds (*Setaria viridis*, *Eleusine indica*, rice, *Portulaca oleracea*, *Medicago sativa* L., and clover). The test was studied using the same method used for the evaluation of herbicidal activity.

Author contributions

Synthesis and characterization, Y. Q. H., P. P. L.; herbicidal activity evaluation, F. G. Y., Z. Q. G., J. X. W., Z. Q. Z.; writing, review and editing, Y. Q. H, H. Y. L., D. Z. H., Y. F. All authors have read and agree to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: IR, ^{1}H NMR, ^{13}C NMR, and HRMS spectra for all compounds, and herbicidal effects of compounds against tested weeds. See DOI: https://doi.org/10.1039/d5ra05630f.

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