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Synthesis and Herbicidal Activities of *p*-Menth-3-en-1-amine and Its Schiff Base Derivatives

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ABSTRACT: *p*-Menth-3-en-1-amine, **4**, and its Schiff base derivatives, **5a**–**l**, were designed and synthesized. They were characterized by FT-IR, ESI$^+$-MS, HRMS, ^{1}H NMR, and ^{13}C NMR spectral analyses, and their pre-emergence herbicidal activities against ryegrass were evaluated. All the compounds showed excellent herbicidal activity. The Schiff bases showed stronger herbicidal activities than the original amine **4**. These compounds showed comparable herbicidal activities to glyphosate. The herbicidal activities of **5k** and **5l** against ryegrass shoot growth were 78.3% and 355.6% higher than that of glyphosate, respectively. Furthermore, the introduction of a chlorine or bromine atom into the Schiff base derivatives containing a furan or benzene ring was beneficial to increase the activity. However, the herbicidal activities were not clearly affected when the heteroatom of the five-membered heterocyclic Schiff base or the position of the substituent on pyridine Schiff base was altered.

KEYWORDS: *p*-menth-3-en-1-amine, Schiff base derivatives, botanical herbicides, herbicidal activity

INTRODUCTION

Herbicides are widely applied in agriculture to eliminate weeds, mainly in wheat, rice, potato, cotton, paddy, and corn fields around the world.[1–6] According to the FAO statistics, sustained herbicide use increased the annual global food production by >10%.[7] However, with the extensive use of traditional herbicides, the occurrence of herbicide-resistant weeds has increased rapidly during the past three decades.[8–10] Furthermore, the use of traditional herbicides has created other problems such as toxicity to nontarget organisms and environmental contamination.[11–13] To solve these problems, it is important to explore some novel eco-friendly herbicides. Botanical herbicides have attracted much attention because of their excellent biological activities and eco-friendly characteristics.[14–16] Compared to traditional chemical pesticides, botanical herbicides have many advantages. They are easily degraded by natural microbes and cannot accumulate in the environment because of rapid degradation by healthy plant tissues.[17] Most importantly, they have a low toxicity to mammals.[18]

The application of monoterpene derivatives in agricultural systems has increased because of their unique herbicidal activity. The commercial herbicide cinmethylin is one of the most important cineole herbicides; it inhibits the meristematic growth of many annual grass weeds.[19] Schiff base derivatives exhibit various bioactivities such as herbicidal, antibacterial, and antitumor activities.[20–22] Most importantly, Schiff base derivatives containing an azomethine group undergo transamination and racemization reactions in biological systems.[23,24] According to the principle of superposition of biological activity, excellent herbicidal activity has been predicted for monoterpene heterocyclic Schiff base compounds.[25] Based on the above characteristics, a series of novel monoterpene (*p*-menth-3-en-1-amine) Schiff base derivatives were designed and synthesized as potential botanical herbicides.

MATERIALS AND METHODS

Materials. NMR spectra were recorded on an Avance III 500 MHz spectrometer (Bruker, Fällanden, Switzerland) using DMSO-d_6 as the solvent and TMS as the internal reference. FT-IR spectra were recorded using a Nicolet IS10 IR instrument (Thermo Fisher Scientific, Waltham, MA) connected to an OMNIC operating system. ESI^+-MS analyses were carried out using a TSQ Quantum ultra AM mass spectrometer (Thermo Finnigan, San Jose, CA). The HRMS analyses were performed using a VS PDO3 mass spectrometer (Agilent, Palo Alto, CA) under electron spray ionization. Melting points were recorded using a WRS-1B digital melting point apparatus (Shen Guang, Shanghai, China). GC analysis was carried out using a GC-2014AF (Shimadzu, Kyoto, Japan) with a HP-5 quartz capillary column (D. 30 m x 0.25 mm, df 0.25 μm). GC separation conditions were as follows: Injection temperature, 270 °C; detector temperature, 270 °C; carrier gas, nitrogen; flow rate, 3.0 mL/min; detector, FID; temperature program: 70 °C, held for 2 min; 3 °C/min to 100 °C then 10 °C to 270 °C, held for 2 min. Column chromatography was carried out on a 305 x 40 mm column of silica gel (200-300 mesh). Terpin (*p*-menthane-1,8-diol) was prepared following a literature procedure.[26] Other reagents were analytically pure and obtained commercially from Shanghai Jingchun

Biochemical Technology Co. Ltd. (Shanghai, China) and used as received without further purification.

Synthesis of *N,N′*-diacetyl-*p*-menthane-1,8-diamine. General Procedure. *N,N′*-diacetyl-*p*-menthane-1,8-diamine was synthesized using Ritter-type conditions according to a reported method.[27] First, 48 mL 60% H_2SO_4 and 23.8 g terpin were added to a flask, and then 59.2 mL acetonitrile was added dropwise to the reaction mixture using a constant pressure funnel. The mixture was heated using an oil bath under continuous stirring using a magnetic stirrer. The temperature of the reaction mixture was increased slowly to 75 °C. The reaction was maintained at this temperature for 8 h and then cooled to room temperature (25 °C). The reaction mixture was poured into 200 mL water, and the solution was adjusted to pH 7 with 20% aqueous NaOH solution. Then, the solution was transferred to a separatory funnel (1000 mL) and extracted twice with 100 mL ethyl acetate. The organic phase was concentrated to obtain a yellow viscous solid using a vacuum rotatory evaporator at 50 °C; the solid was washed with ethyl acetate, affording 19.2 g *N,N′*-diacetyl-*p*-menthane-1,8-diamine, **2**, (n_{trans}:n_{cis} = 4:1) in 57.3% yield. Next, 19.2 g *N,N′*-diacetyl-*p*-menthane-1,8-diamine and 100 mL ethyl acetate were added to a flask equipped with a condenser. The solution was stirred using a magnetic stirrer and refluxed until **2** was completely dissolved in ethyl acetate. Then, the solution was transferred into a 100-mL beaker; white crystals precipitated after a day. 14.2 g *trans*-*N,N′*-Diacetyl-*p*-menthane-1,8-diamine, **2a**, was obtained after suction filtration and vacuum drying (60 °C). The filtrate was concentrated to obtain a yellow viscous solid. By repeating the above steps, 3 g *cis*-*N,N′*-diacetyl-*p*-menthane-1,8-diamine, **2b**, was obtained.

Synthesis of *p*-menth-3-en-1-amine. First, 451.4 mL of 7.5% aqueous HCl was stirred in a flask at room temperature (25 °C). Then, 101.6 g (0.4 mol) *N,N′*-diacetyl-*p*-menthane-1,8-diamine, **2**, was added. The reaction mixture was refluxed for 8 h using a heating mantle. Then, the reaction mixture was cooled to room temperature (25 °C). The solution of the upper layer was concentrated using a rotary vacuum evaporator, affording a yellow viscous material (43 g, crude product of **3**). The experiment was repeated three times. The residues were combined. Next, 64.9 g of the crude product of **3** was transferred to another flask equipped with a thermometer and condenser-west tube. Then, 300 mL of ethylene glycol and 20 g of NaOH were added. To remove the low-boiling substances, the reaction mixture was refluxed until the temperature reached 170 °C. Then, the reaction mixture was cooled to room temperature (25 °C), and the condenser-west tube was replaced with a condenser-Allihn type. The reaction mixture was refluxed for 13 h and then cooled to room temperature (25 °C). The reaction mixture was transferred to a separatory funnel (1000 mL) containing 100 mL water and extracted four times with 100 mL ethyl acetate. The organic phase was added to 200 mL H_2O, and adjusted to pH 4–6 with dilute HCl. Then, the aqueous phase was adjusted to pH 9–10 with a NaOH solution; 23.3 g (0.15 mol) *p*-menth-3-en-1-amine, **4**, was obtained after the distillation of the organic phase.

Synthesis of Schiff base derivatives of *p*-menth-3-en-1-amine. First, 20 mL absolute alcohol was added to a flask. Then, 4 mmol *p*-menth-3-en-1-amine and 4.8 mmol of the corresponding aldehyde were added to the flask. The reaction mixture was stirred using a magnetic stirrer at room temperature (25 °C) for 2–96 h. The reaction progress was monitored by TLC. When the reaction was completed, the solvent was removed using a vacuum evaporator. The crude products were purified by column chromatography on silica gel, affording the Schiff base derivatives of *p*-menth-3-en-1-amine.

trans-*N,N′*-diacetyl-p-menthane-1,8-diamine, **2a**, was recovered in 42% yield as a white solid, m.p. 196.5-197 °C. HRMS (ESI) for $C_{14}H_{27}N_2O_2$, calcd. 255.2067; found 255.2065 $[M+H]^+$, $\Delta = 0.77$ ppm.

cis-*N,N′*-diacetyl-*p*-menthane-1,8-diamine, **2b**, was recovered in 9% yield as a white solid, m.p. 245.2-246.2 °C. HRMS (ESI) for $C_{14}H_{27}N_2O_2$, calcd. 255.2067; found 255.2064 $[M+H]^+$, $\Delta = 1.02$ ppm.

p-menth-3-en-1-amine, **4**, was recovered in 13% yield as a colorless transparent liquid, b.p. 183.96 °C. HRMS (ESI) for $C_{10}H_{20}N$, calcd. 154.1590, found 154.1590 $[M+H]^+$, $\Delta =0.01$ ppm.

N-(furan-2-ylmethylene)-4-isopropyl-1-methylcyclohex-3-enamine, **5a**, was recovered in 97% yield as a yellow viscous liquid. HRMS (ESI) for $C_{15}H_{22}NO$, calcd. 232.1696, found 232.1713 $[M+H]^+$, $\Delta =3.15$ ppm.

4-isopropyl-1-methyl-*N*-((5-methylfuran-2-yl)methylene)cyclohex-3-enamine, 5**b**, was recovered in 96% yield as a yellow viscous liquid. HRMS (ESI) for $C_{16}H_{24}NO$, calcd. 246.1852, found 246.1878 $[M+H]^+$, $\Delta =10.27$ ppm.

(5-(((4-isopropyl-1-methylcyclohex-3-en-1-yl)imino)methyl)furan-2-yl)methanol, **5c**, was recovered in 87% yield as a yellow viscous liquid. HRMS (ESI) for $C_{16}H_{24}NO_2$, calcd. 262.1802, found 262.1819 $[M+H]^+$, Δ =6.58 ppm.

N-((5-bromofuran-2-yl)methylene)-4-isopropyl-1-methylcyclohex-3-enamine, **5d**, was recovered in 98% yield as a yellow viscous liquid. HRMS (ESI) for $C_{15}H_{21}NOBr$, calcd. 310.0801, found 310.0805 $[M+H]^+$, Δ =1.34 ppm.

N-((1H-pyrrol-2-yl)methylene)-4-isopropyl-1-methylcyclohex-3-enamine, **5e**, was recovered in 65% yield as a yellow viscous liquid. HRMS (ESI) for $C_{15}H_{23}N_2$, calcd. 231.1856, found 231.1842 $[M+H]^+$, Δ =5.83 ppm.

4-isopropyl-1-methyl-*N*-(thiophen-2-ylmethylene)cyclohex-3-enamine, **5f**, was recovered in 98% yield as a yellow viscous liquid. HRMS (ESI) for $C_{15}H_{22}NS$, calcd. 248.1467, found 248.1478 $[M+H]^+$, Δ =4.22 ppm.

4-isopropyl-1-methyl-*N*-(pyridin-2-ylmethylene)cyclohex-3-enamine, **5g**, was recovered in 99% yield as a yellow viscous liquid. HRMS (ESI) for $C_{16}H_{23}N_2$, calcd. 243.1856, found 243.1863 $[M+H]^+$, Δ =3.01 ppm.

4-isopropyl-1-methyl-*N*-(pyridin-3-ylmethylene)cyclohex-3-enamine, **5h**, was recovered in 88% yield as a yellow viscous liquid. HRMS (ESI) for $C_{16}H_{23}N_2$, calcd. 243.1856, found 243.1863 $[M+H]^+$, Δ =3.01 ppm.

4-isopropyl-1-methyl-*N*-(pyridin-4-ylmethylene)cyclohex-3-enamine, **5i**, was recovered in 90% yield as a yellow viscous liquid. HRMS (ESI) for $C_{16}H_{23}N_2$, calcd. 243.1856, found 243.1861 $[M+H]^+$, Δ =2.30 ppm.

N-benzylidene-4-isopropyl-1-methylcyclohex-3-enamine, **5j**, was recovered in 92%

yield as a yellow viscous liquid. HRMS (ESI) for $C_{17}H_{24}N$, calcd. 242.1909, found 242.1913 $[M+H]^+$, Δ =1.70 ppm.

N-(4-chlorobenzylidene)-4-isopropyl-1-methylcyclohex-3-enamine, **5k**, was recovered in 90% yield as a yellow viscous liquid. HRMS (ESI) for $C_{17}H_{23}ClN$, calcd. 276.1514, found 276.1533 $[M+H]^+$, Δ =6.67 ppm.

N-(2,6-dichlorobenzylidene)-4-isopropyl-1-methylcyclohex-3-enamine, **5l**, was recovered in 86% yield as a yellow viscous liquid. HRMS (ESI) for $C_{17}H_{22}Cl_2N$, calcd. 310.1124, found 310.1120 $[M+H]^+$, Δ =1.23 ppm.

Herbicidal activity against ryegrass. Annual ryegrass seed was selected as the test plant seed for this assay. First, 2 mmol of each compound was dissolved in 0.25 mL DMF in a 100-mL volumetric flask. Then, a drop of Tween-80 was added as the emulsification reagent to the volumetric flask and diluted with distilled water to 20 $mmol·L^{-1}$. Then, the concentrates were diluted with the control solution (2.5 mL DMF and 10 drops of Tween-80 in 1 L distilled water) to 10, 5, 2.5, 1.25, 0.625, and 0.3125 mmol/L. The seeds were soaked in warm water (25 °C) for 15 h before use. Then, 10 mL of the solution of test compounds of each concentrate and 10 mL of the control solution were added to the corresponding Petri dishes (9 cm in diameter) lined with a filter paper (9 cm in diameter). Then, 10 seeds were added to each of the Petri dishes (at each concentration), and for the controls, three replicates were used) and cultivated in the dark at 25 °C for 5 days. The inhibition rate was calculated according to the equation:

$$y = \frac{x_2 - x_1}{x_2}$$

Where: y is the inhibition rates of the root or shoot growth; x_2 is the root or shoot length of the blank control group; x_1 is the root or shoot length of the group treated with the test compounds.

RESULTS AND DISCUSSION

Synthesis of *p*-menth-3-en-1-amine. The monoterpene derivatives with a *p*-menthene skeleton are one of the most important bioactive compounds.[28] Thus, it is important to exploit the related compound **4**. To develop an efficient synthetic method for compound **4**, compound **2** was hydrolyzed with NaOH or HCl under various conditions. No product was obtained when compound **2** was treated with a NaOH aqueous solution. When treated with a NaOH solution of ethylene glycol at higher than 170 °C (reaction temperature) for 13 h, compound **2** was hydrolyzed with a high conversion. However, the main product was *p*-menthane-1,8-diamine. When the reaction time was prolonged, the amino group in the C^8 position of *p*-menthane-1,8-diamine could not be eliminated, and compound **4** could not be obtained.

Compound **3** was obtained when compound **2** was hydrolyzed with a 7.5% HCl (wt.) aqueous solution for 8 h. Even if the reaction time was prolonged, compound **4** could not be obtained. However, when compound **3** was hydrolyzed with a NaOH solution of ethylene glycol at >170 °C for 13 h, compound **4** was obtained. Moreover, the conversion rate of compound **3** was almost 100%, and only a few byproducts

(<1%) were produced.

Synthesis of Schiff base derivatives of *p*-menth-3-en-1-amine. During our investigation, we found that compound **4** easily reacted with aldehydes *via* nucleophilic addition reaction, and the reaction could be carried out at room temperature (25 °C) in ethyl alcohol as the solvent. When compound **4** was treated with aldehydes in an ethyl alcohol aqueous solution under mild conditions (reaction temperature: 25 °C, normal pressure), the Schiff base derivatives of compound **4** were obtained in 65–99% yields. The electron density of the carbonyl of furfural is lower than those of pyrrole-2-carboxaldehyde and thiophene-2-carbaldehyde;[29] therefore, the carbonyl group of furfural is more easily attacked by nucleophilic reagents (compound **4**), improving the reactivity of furfural. For example, the reaction of furfural with *p*-menth-3-en-1-amine in ethanol as the solvent was completed under stirring using a magnetic stirrer at room temperature (25 °C) in only 2 h. However, the reaction of thiophene-2-carbaldehyde with compound **4** was completed under the same conditions in >96 h.

Herbicidal activity. The pre-emergence herbicidal activities of the Schiff base derivatives of *p*-menth-3-en-1-amine, **4**, against ryegrass were determined, and the commercial herbicide glyphosate was selected as the positive control.

The results were listed in Tables 1 and 2. Compound **4** and its Schiff base derivatives (**5**) showed excellent herbicidal activities. The herbicidal activities of these compounds were much higher than those of **2a** and **2b** (>15 times) by comparing the values (the IC_{50} of glyphosate against ryegrass root growth/the IC_{50} of test compound against ryegrass root growth or the IC_{50} of glyphosate against ryegrass shoot growth/the IC_{50} of test compound against ryegrass shoot growth) (Table 2). The growth of the root and shoot were both completely inhibited when the concentrations of compound **4** and its derivatives were 5 $mmol \cdot L^{-1}$. The IC_{50} and IC_{90} of compound **4** and its Schiff base derivatives against ryegrass root and shoot growth were lower than 0.6 $mmol \cdot L^{-1}$ and 1.7 $mmol \cdot L^{-1}$, respectively. In contrast, the IC_{50} of **2a** and **2b** against ryegrass root and shoot growth were higher than 5 $mmol \cdot L^{-1}$.

Compound **4** and its Schiff base derivatives showed somewhat lower herbicidal activities to glyphosate. The herbicidal activities of these compounds against ryegrass root and shoot growths were higher than 40-80% of the corresponding herbicidal activities of glyphosate, respectively. Some compounds showed much higher herbicidal activities than glyphosate (Figures 4 and 5). For example, the herbicidal activities of **5k** and **5l** against ryegrass root growths were 16.7% and 100.0% higher than that of glyphosate, respectively (Figure 3). Moreover, seven Schiff base derivatives exhibited higher herbicidal activities against ryegrass shoot growth than glyphosate. Further, the herbicidal activities of **5k** and **5l** against ryegrass shoot growth were 78.3% and 355.6% higher than that of glyphosate, respectively (Figure 4).

The herbicidal activities increased when compound **4** was transformed into the corresponding Schiff base derivatives (Figures 3 and 4). Six and nine of the Schiff base derivatives exhibited higher herbicidal activities against ryegrass root and shoot growths than compound **4**, respectively. Further, the other Schiff base derivatives exhibited herbicidal activities similar to compound **4**. The herbicidal activities of compounds **5k** and **5l** against ryegrass shoot growths were 100.1% and 411.3% higher than that of compound **4**, respectively.

Furthermore, it was found that the presence of suitable functional groups in the Schiff base derivatives were essential for high herbicidal activities. The introduction of a chlorine or bromine atom into the Schiff base derivatives containing a furan or benzene ring was beneficial for the herbicidal activity (Figures 3 and 4). The herbicidal activity of compound **5d** (obtained by introducing bromine into compound **5a**) against ryegrass shoot growth was 61.1% higher than **5a**. The herbicidal activity of compound **5k** (obtained by introducing chlorine into compound 5**j**) against ryegrass shoot growth was 175.2% higher than **5j.** However, the herbicidal activities were not clearly affected when the type of heteroatom of the five-membered heterocyclic Schiff base or the position of substituent on pyridine Schiff base was altered.

Monoterpenes and their derivatives generally have a low toxicity. Monoterpenes (α-pinene and β-pinene) are used as the raw materials in the preparation of some spices.[30] The acute toxicity of bornyl benzoate (a monoterpene derivative) on mice was investigated. No adverse effect was observed after the oral administration of this drug; no effect was observed on the normal growth period of mice.[31] This indicates that bornyl benzoate is rather safe. Moreover, monoterpenes were easily degraded in soil-slurry systems.[32] Therefore, the monoterpene derivatives (the Schiff base derivatives of *p*-menth-3-en-1-amine) may not be harmful to humans and animals when they are used as botanical herbicides.

In conclusion, a series of the Schiff base derivatives of *p*-menth-3-en-1-amine were rationally designed and evaluated for their potentials as botanical herbicides. Most of the synthesized compounds displayed excellent herbicidal activities against ryegrass root and shoot growths, and some of them were superior to the commercial herbicide glyphosate. The IC_{50} of these compounds against ryegrass root and shoot growths were 0.07–0.33 and 0.09–0.49 mmol/L, respectively. Compound **5l** exhibited the highest herbicidal activity against ryegrass. The IC_{50} of this compound against ryegrass root and shoot growths were 0.07 $\text{mmol}\cdot\text{L}^{-1}$ and 0.09 $\text{mmol}\cdot\text{L}^{-1}$, respectively. In the future, we will study the toxicity of these herbicidal compounds in animals. Furthermore, we will study the bacteriostatic, insecticidal, and antineoplastic activities of these compounds.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information

The FT-IR, ESI$^+$-MS, and ^{13}C NMR data and spectrum for compounds supplied as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure captions

Figure 1. Synthetic route for the Schiff base derivatives of *p*-menth-3-en-1-amine (**4**). Terpinol refers to terpin, **1**. Reagents and conditions: (a) 60% H_2SO_4, CH_3CN, 75 °C; (b) 10% HCl, reflux; (c) NaOH, ethylene glycol, reflux; (d) RCHO, CH_3CH_2OH, room temperature (25 °C).

Figure 2. Chemical structures of Schiff base derivatives of *p*-menth-3-en-1-amine (**5a-l**)

Figure 3. The herbicidal activities of Schiff base derivatives of *p*-menth-3-en-1-amine against annual ryegrass root growth compared to that of glyphosate (the IC_{50} of glyphosate/the IC_{50} of the test compound).

Figure 4. The herbicidal activities of Schiff base derivatives of *p*-menth-3-en-1-amine against annual ryegrass shoot growth compared to that of glyphosate (the IC_{50} of glyphosate/the IC_{50} of the test compound).

Tables

Table 1. Herbicidal Activities of Schiff Base Derivatives of *p*-Menth-3-en-1-amine Against Annual Ryegrass

compd.	Inhibition rate (%) of root growth at different solution concentrations (mmol/L)						Inhibition rate (%) of shoot growth at different solution concentrations (mmol/L)					
	5	2.5	1.25	0.625	0.3125	0.1563	5	2.5	1.25	0.625	0.3125	0.1563
2a	31.0	19.8	14.8	10.7	6.8	3.4	30.3	20.6	14.0	9.2	5.7	3.2
2b	45.9	17.8	14.3	7.8	6.6	3.3	33.7	15.2	5.3	6.1	3.5	2.6
4	100	100	100	92.2	50.4	37.6	100	100	89.5	50.0	29.9	19.4
5a	100	100	98.2	83.1	53.5	20.3	100	100	71.9	53.9	30.2	14.4
5b	100	100	89.7	55.1	54.3	33.6	100	87.5	53.5	40.5	31.3	27.5
5c	100	100	96.4	62.9	52.3	38.1	100	92.2	74.9	38.3	18.6	18.4
5d	100	100	100	87.4	66.0	53.0	100	100	87.1	67.1	56.6	40.1
5e	100	100	99.5	87.7	63.9	40.9	100	100	91.6	51.9	41.2	36.5
5f	100	100	97.1	79.5	49.5	29.2	100	97.4	69.6	60.6	37.1	19.3
5g	100	100	99.4	93.6	80.3	21.6	100	100	80.9	66.5	48.5	20.8
5h	100	100	100	92.1	86.4	11.1	100	100	94.2	53.5	32.9	11.9
5i	100	100	100	82.0	41.8	6.5	100	100	83.1	43.3	33.5	14.4
5j	100	100	88.1	77.2	46.4	19.4	100	93.8	72.2	51.3	29.5	13.9
5k	100	100	100	99.1	84.1	62.9	100	100	100	78.0	42.1	37.7
5l	100	100	100	100	100	69.1	100	100	100	100	97.8	45.6
glyphosate	100	100	100	95.7	80.1	65.5	100	100	99.6	90.6	41.0	0.2

When the solution concentration was 0.0781 mmol·L^{-1}, the inhibition rate of compound **5l** against ryegrass root and shoot growth were 39.5% and 28.8%, respectively.

When the solution concentration was 0.0391 mmol·L^{-1}, the inhibition rate of compound **5l** against ryegrass root and shoot growth were 25.8% and 20.3%, respectively.

Table 2. IC_{50} and IC_{90} of Schiff Base Derivatives of *p*-Menth-3-en-1-amine Against Annual Ryegrass

compd.	root		shoot	
	IC_{50} mmol/L	IC_{90} mmol/L	IC_{50} mmol/L	IC_{90} mmol/L
2a	>5	>5	>5	>5
2b	>5	>5	>5	>5
4	0.24	0.40	0.46	1.66
5a	0.29	0.58	0.41	0.78
5b	0.31	0.64	0.49	1.24
5c	0.29	0.59	0.51	1.18
5d	0.18	0.38	0.29	0.61
5e	0.23	0.46	0.32	0.66
5f	0.29	0.59	0.43	1.01
5g	0.23	0.48	0.34	0.69
5h	0.21	0.42	0.38	0.73
5i	0.29	0.42	0.40	0.77
5j	0.33	0.66	0.48	1.12
5k	0.12	0.27	0.23	0.46
5l	0.07	0.12	0.09	0.17
glyphosate	0.14	0.30	0.41	0.70

Figure graphics

Figure 1.

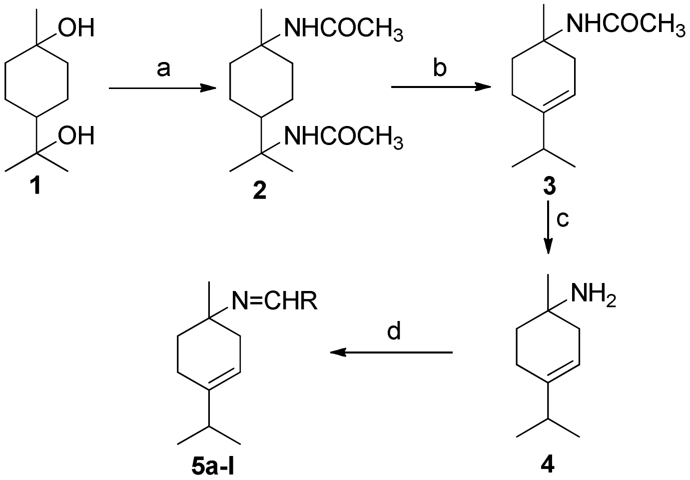
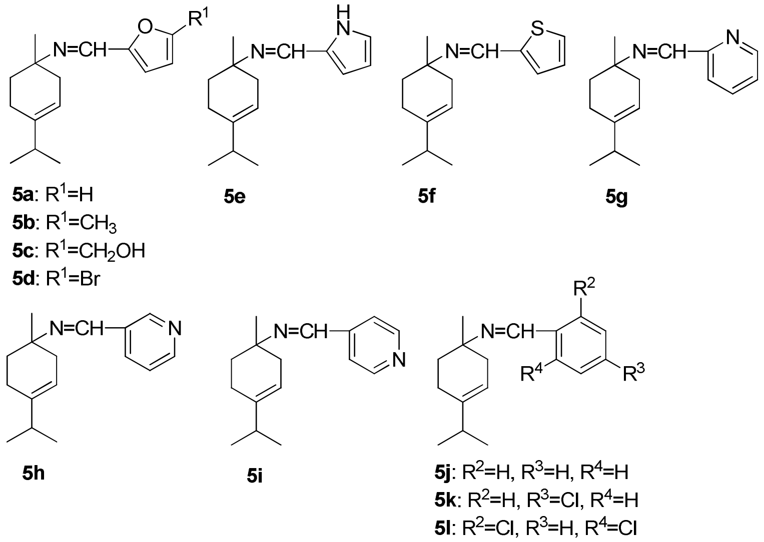


Figure 2.



5a: R^1=H
5b: R^1=CH$_3$
5c: R^1=CH$_2$OH
5d: R^1=Br

5e

5f

5g

5h

5i

5j: R^2=H, R^3=H, R^4=H
5k: R^2=H, R^3=Cl, R^4=H
5l: R^2=Cl, R^3=H, R^4=Cl

Figure 3.

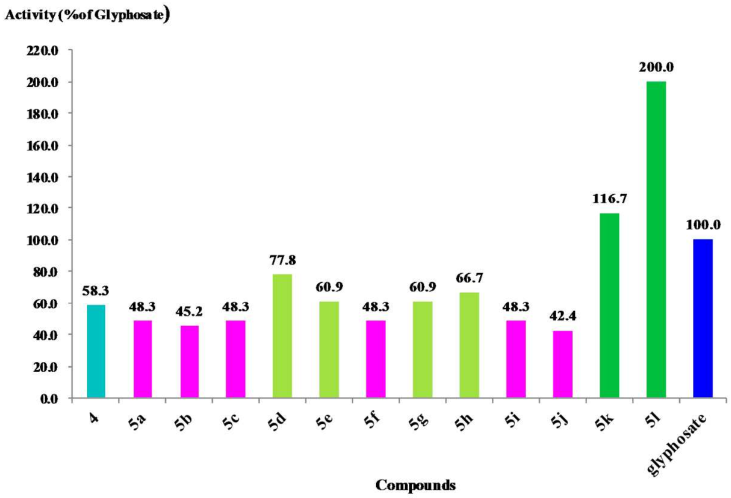

Activity (%of Glyphosate)
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
58.3
48.3
45.2
48.3
77.8
60.9
48.3
60.9
66.7
48.3
42.4
116.7
200.0
100.0
4
5a
5b
5c
5d
5e
5f
5g
5h
5i
5j
5k
5l
glyphosate
Compounds

Figure 4.

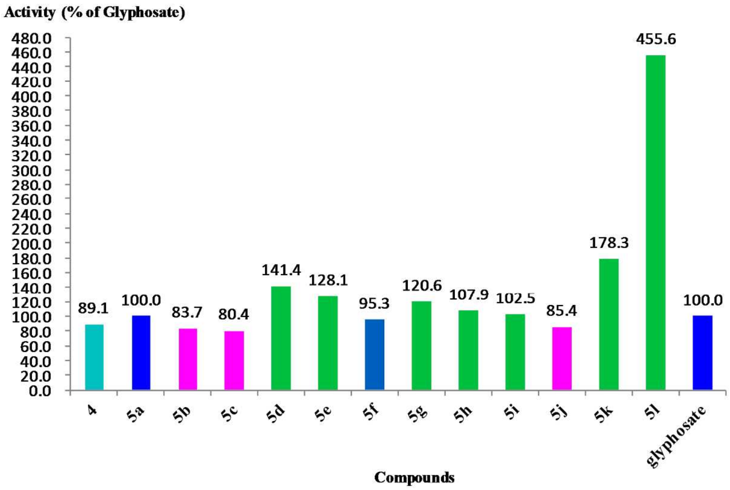
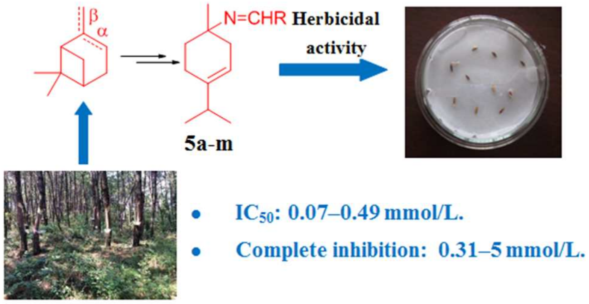

Activity (% of Glyphosate)
480.0
460.0
440.0
420.0
400.0
380.0
360.0
340.0
320.0
300.0
280.0
260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
89.1
100.0
83.7
80.4
141.4
128.1
95.3
120.6
107.9
102.5
85.4
178.3
455.6
100.0
4
5a
5b
5c
5d
5e
5f
5g
5h
5i
5j
5k
5l
glyphosate
Compounds

Table of Contents Graphics

(For Table of Contents only)



- IC$_{50}$: 0.07–0.49 mmol/L.
- Complete inhibition: 0.31–5 mmol/L.