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The synthesis of novel oxime ethers and their effects on the senescence of cut carnation flowers

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Abstract The high levels of ethylene in plants are involved in a range of harmful effects, such as the senescence of plants and the rotting of fruits. A series of novel oxime ethers were synthesized to counteract the ethylene effects. Their structures were characterized by IR, MS, and ^{1}H NMR, and their effects on the senescence of cut carnation flowers were investigated. The results show that all of the target compounds extended the vase life of cut carnation, especially for compound **3i**, which prolonged the vase life of cut carnation flowers to about 11 days, nearly 75% longer vase life compared to the control groups. Most of them were more effective than $AgNO_3$ and aminooxyacetic acid.

Keywords Ethylene inhibitor · Oxime · Cut carnation · Senescence

Introduction

Ethylene plays an important role in a wide range of aspects of plant growth and development, such as promoting the germination of seeds, the differentiation of tissues, the expansion of stems and the growth of roots, the formation of adventitious roots, and the ripening of fruits [1–3]. Certain periods of plant growth, for example, seeds germination, fruits after-ripening, leaves falling, and flowers senescence, will induce ethylene formation, which, in turn, the accumulation of ethylene will further stimulate the production of ethylene.

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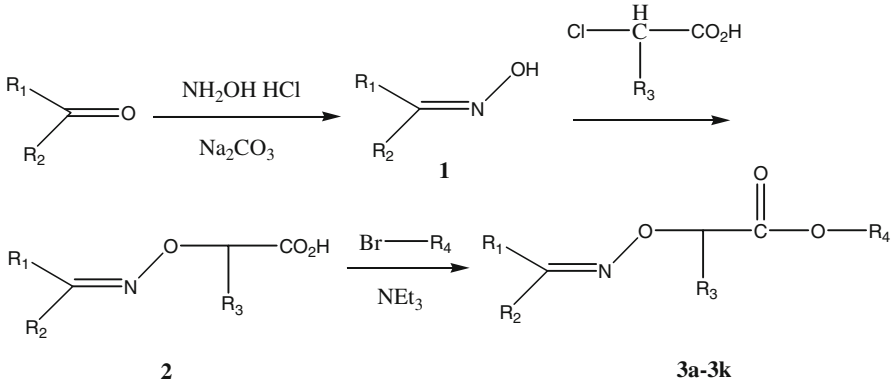
High levels of ethylene in plants can result in many deleterious effects, especially for the acceleration of the senescence of plants and the rotting of fruits, so ethylene inhibitors are strongly needed in order to preserve agricultural products [4, 5]. Inhibitors of ethylene action and inhibitors of ethylene biosynthesis are two kinds of typical ethylene inhibitors [6]. Common inhibitors of ethylene action include silver ions (e.g., silver thiosulfate, STS), 2,5-norbornadiene (NBD), diazocyclopentadiene (DACP), and cyclopropene derivatives. Ethylene action inhibitors compete with ethylene for the binding receptor to counteract ethylene effects [7–10]. The practical use of STS is limited because it is environmentally critical [11, 12]. NBD, DACP, and cyclopropene derivatives are gas per se; the inconvenience and the hidden safety dangers for operation makes their practical uses limited [13].

Familiar ethylene biosynthesis inhibitors include aminooxyacetic acid (AOA), aminoethoxyvinylglycine (AVG), and methoxyvinylglycine (MVG). These inhibitors are able to block the pathway of ethylene biosynthesis, leading to a low ethylene level in plants [14, 15]. AVG and MVG are difficult to be prepared, and, thus, too expensive for practical use; additionally, their phytotoxicity is also a problem [16, 17].

The intensive pungent smell of AOA makes it unacceptable for practical use [18, 19]. Therefore, people managed to synthesize some oxime ether derivatives of AOA (see Scheme 1). Inspired by this, a series of novel oxime ether derivatives of AOA were designed and synthesized (see Fig. 1), and their effects on the senescence of cut carnation flowers were investigated in this article.



Scheme 1 The synthesis route. **3a** $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = H$, $R_4 = CH(CH_3)CO_2Et$; **3b** $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = H$, $R_4 = CH_2CO_2Et$; **3c** $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = H$, $R_4 = (CH_2)_3CO_2Et$; **3d** $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = CH_3$, $R_4 = CH_2CO_2Et$; **3e** $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = CH_3$, $R_4 = CH(CH_3)CO_2Et$; **3f** $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = CH_3$, $R_4 = (CH_2)_3CO_2Et$; **3g** $R_1 = Ph$, $R_2 = H$, $R_3 = H$, $R_4 = CH_2CO_2Et$; **3h** $R_1 = Ph$, $R_2 = H$, $R_3 = H$, $R_4 = CH(CH_3)CO_2Et$; **3i** $R_1 = Ph$, $R_2 = H$, $R_3 = H$, $R_4 = (CH_2)_3CO_2Et$; **3j** $R_1 = Ph$, $R_2 = H$, $R_3 = CH_3$, $R_4 = CH_2CO_2Et$; **3k** $R_1 = Ph$, $R_2 = H$, $R_3 = CH_3$, $R_4 = CH(CH_3)CO_2Et$

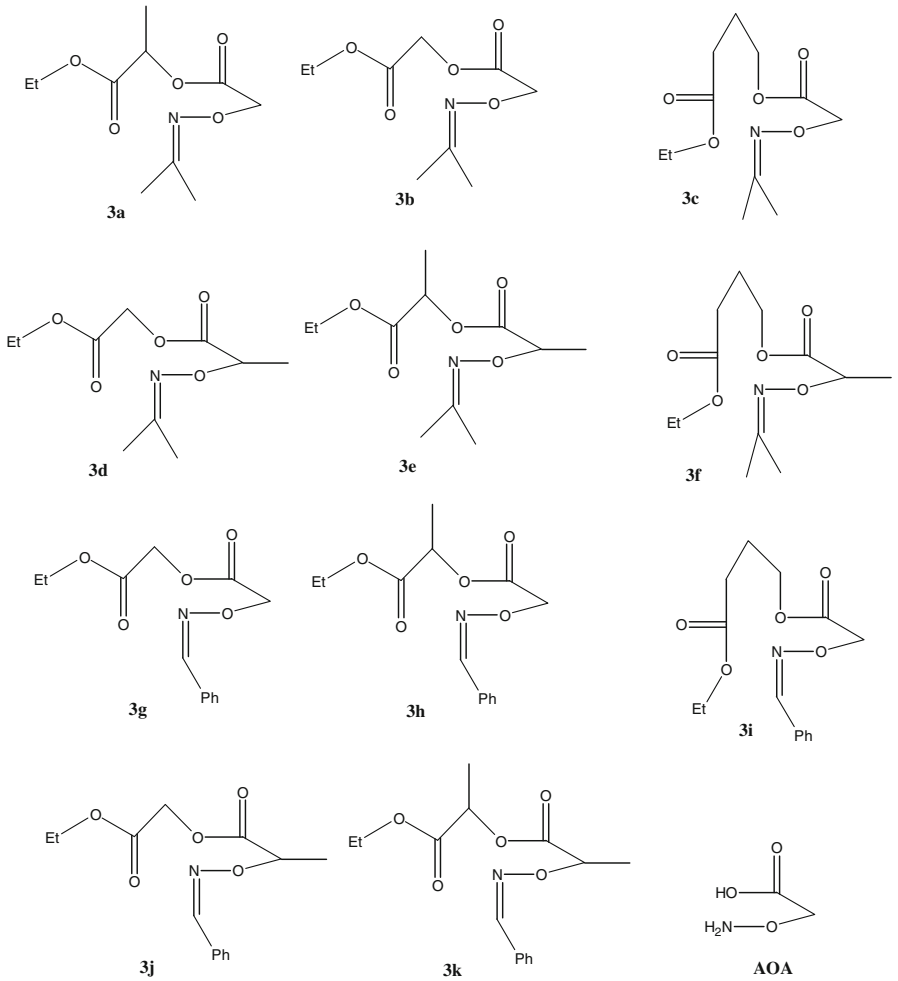


Fig. 1 The structure of the synthesized compounds

Results and discussion

Synthesis

For the synthesis of compound **2**, which was prepared by the reaction of the corresponding oxime **1** and halocarboxylic acid, chlorocarboxylic acid gave a poorer yield, while bromocarboxylic acid behaved much better, so bromocarboxylic acid is recommended to be used in the preparation of compound **2**. The temperature should be controlled at around 0 °C. When the temperature was higher, the side reaction between halocarboxylic acids themselves would take place, that is, the acyloxy anion group of one molecule could attack the halo-bearing carbon of another halocarboxylic acid molecule.

For the preparation of **3a–3k** by the reaction of carboxymethoxime **2** with halocarboxylic acid ester, triethylamine was used as the acid binding agent. The hydroxyl group of metal base would attack the halo atom of the halocarboxylic acid ester and replace the halo atom, so it is unadvisable to use metal base in this step.

Effect of oxime ethers on the preservation of cut carnation flowers

In preliminary experiments, the concentration (100 mg/L) of **3a** that sufficed to extend flower vase life was selected. According to the literature, 0.2 mM STS concentration was recommended to extend vase life [20]. It was also reported that the application of 1.0 mM AOA caused chemical injury to the cut flowers, but 0.1 mM AOA did not [21]. Accordingly, the concentration of $AgNO_3$ and AOA applied in this work were 50 and 70 mg/L, respectively. Table 1 describes their influence on the senescence of cut carnation flowers. Compared to the control group, the vase life of cut carnation flowers treated with **3a–3k** was significantly prolonged. Especially for compounds **3b**, **3c**, **3e**, **3f**, **3h**, and **3i**, all of them prolonged the vase life by more than 50%. 50 mg/L silver ion treatment extended the vase life of cut carnation by about 30.8%, and AOA extended the vase life by nearly 40% longer than the control. So, compounds **3b**, **3c**, **3e**, **3f**, **3h**, and **3i** were more effective than 70 mg/L AOA and 50 mg/L $AgNO_3$. The common structural feature of **3b**, **3c**, and **3i** was that R_4 is a straight line when R_3 was H. Especially for **3i** and **3c**, which were the best in each subset, they shared the same substructure of R_4 (i.e., ethyl butanoate). For **3e** and **3f**, which also demonstrated high activities, R_4 was a carboxylic acid with more than two carbons when R_3 was CH_3. However, it is only a preliminary conclusion. This suggests that the structure of R_3 and R_4 likely plays an important role in the mechanism of their action.

Table 1 Influence of compounds on the vase life of cut carnation flowers

Compound	Concentration (mg/L)	Vase life (days)	Prolongation rate (%)
CK (DBS)	0.1%	14.3 ± 0.8^{f}	–
AOA	70	20.0 ± 0.5^{d}	39.9
$AgNO_3$	50	18.7 ± 0.8^{de}	30.8
3a	100	20.0 ± 0.7^{d}	39.9
3b	100	23.0 ± 0.9^{bc}	60.8
3c	100	23.0 ± 1.0^{bc}	60.8
3d	100	17.5 ± 1.1^{e}	22.4
3e	100	23.5 ± 0.6^{b}	64.3
3f	100	22.0 ± 1.0^{c}	53.8
3g	100	18.0 ± 0.7^{e}	25.9
3h	100	22.0 ± 0.8^{c}	53.8
3i	100	25.0 ± 0.5^{a}	74.8
3j	100	15.5 ± 1.2^{f}	8.4
3k	100	18.0 ± 0.9^{e}	25.9

The values in one column with different letters are significantly different ($p < 0.05$, Duncan's multiple range test). Senescence: the petals have lost turgidity and the flowers are partially closed, advanced inrolling symptoms and browning. The control was 0.1% DBS solution

Conclusion

The title oxime ether derivatives can prolong the vase life of cut carnation flowers and deserve further research as cut flowers preservatives.

Experimental section

The structures were confirmed by an AVATAR 330 Infrared Spectrometer (KBr), a Saturn 2200 Mass Spectrograph, and a Bruker AV400 400-MHz H Nuclear Magnetic Resonance Spectrometer (δ, $CDCl_3$).

Typical procedure for the synthesis of oxime ether derivatives

The synthesis method was exemplified by the preparation of compound **3a**.

Acetoxime **1** was prepared by the direct addition between acetone and hydroxylamine. Acetone carboxymethoxime **2** was prepared by the reaction of acetoxime **1** and chloroacetic acid or bromoacetic acid, according to the literature [22].

3a was prepared by the reaction of acetone carboxymethoxime **2** with ethyl 2-bromopropanoate. Briefly, 1.97 g (0.015 mol) compound acetone carboxymethoxime **2**, 2.1 mL (0.015 mol) triethylamine, and 7.5 mL *N*,*N*-dimethylformamide (DMF) was placed into a two-necked flask. After the mixture was stirred for about 30 min at 20 °C, a solution of 2.72 g (0.015 mol) ethyl 2-bromopropanoate in 10 mL DMF was added dropwise within 1 h. Then, the mixture was reacted at 20 °C for 4 h and at 80 °C for 8 h with stirring. After cooling, the triethylamine hydrobromide was filtered, and then the DMF solvent was removed under reduced pressure; 30 mL chloroform and 15 mL water was added to the residue. The chloroform layer was collected and washed with 10 mL 1 mol/L HCl, 10 mL 5% aqueous $NaHCO_3$, and 10 mL water subsequently. Then, it was dried with anhydrous sodium sulfate. After the removal of chloroform by distillation, the target product was produced as a yellow liquid.

*Ethyl 2-[[2-[[(1-methylethylidene)amino]oxy]acetyl]oxy] propionate (**3a**)*

A light yellow liquid, yield 66.4%. IR (KBr, cm^{-1}), 2,920–2,965 (CH_3), 2,885–2,915 (CH_2), 1,764 (C=O), 1,635 (C=N), 1,120 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.24–1.29 (3H, t, $J = 9.6$ Hz), 1.48–1.50 (3H, d, $J = 9.2$ Hz), 1.86 (3H, s), 1.92 (3H, s), 4.15–4.22 (2H, q, $J = 9.6$ Hz), 4.63 (2H, s), 5.11–5.18 (1H, q, $J = 9.2$ Hz), MS (*m/z*, %): 232 (M^+, 35%), 56 (100%).

*Ethyl 2-[[2-[[(1-methylethylidene)amino]oxy]acetyl]oxy] acetate (**3b**)*

A light yellow liquid, yield 54.1%. IR (KBr, cm^{-1}), 2,955–2,987 (CH_3), 2,875–2,926 (CH_2), 1,759 (C=O), 1,644 (C=N), 1,178 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.23–1.28 (3H, t, $J = 9.6$ Hz, C–CH_3), 1.84 (3H, s, N=C–CH_3), 1.90 (3H, s, N=C–CH_3), 4.15–4.22 (2H, q, $J = 9.6$ Hz, O=C–O–CH_2), 4.63 (2H, s,

O–CH_2–C=O), 4.64 (2H, s, O–CH_2–C=O), MS (*m/z*, %): 218 ($(M+1)^+$, 57%), 56 (100%).

*Ethyl 4-[[2-[[(1-methylethylidene)amino]oxy]acetyl]oxy] butanoate (**3c**)*

A light yellow liquid, yield 60.2%. IR (KBr, cm^{-1}), 2,961–2,983 (CH_3), 2,907–2,927 (CH_2), 1,733 (C=O), 1,644 (C=N), 1,258 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.24–1.28 (3H, t, $J = 7.2$ Hz, C–CH_3), 1.88 (3H, s, N=C–CH_3), 1.93 (3H, s, N=C–CH_3), 1.97–2.00 (2H, t, $J = 7.0$ Hz O–C–CH_2), 2.37–2.41 (2H, t, $J = 7.2$ Hz, O=C–CH_2), 4.13–4.22 (4H, m), 4.56 (2H, s, O–CH_2–C=O), MS (*m/z*, %): 246 ($(M+1)^+$, 13%), 115 (40%), 56 (100%).

*Ethyl 2-[[2-[[(1-methylethylidene)amino]oxy]propionyl]oxy] acetate (**3d**)*

A light yellow liquid, yield 35.2%. IR (KBr, cm^{-1}), 2,964–2,988 (CH_3), 2,879–2,941 (CH_2), 1,757 (C=O), 1,654 (C=N), 1,273 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.26–1.31 (3H, m, C–CH_3), 1.52–1.54 (3H, d, $J = 7.2$ Hz, O–C–CH_3), 1.86 (3H, s, N=C–CH_3), 1.93 (3H, s, N=C–CH_3), 4.19–4.25 (2H, m, O=C–O–CH_2), 4.55–4.59 (1H, q, $J = 5.2$ Hz, O–CH–C=O), 4.74–4.79 (2H, m, O–CH_2–C=O), MS (*m/z*, %): 232 ($(M+1)^+$, 55%), 56 (100%).

*Ethyl 2-[[2-[[(1-methylethylidene)amino]oxy]propionyl]oxy] propionate (**3e**)*

A light yellow liquid, yield 61.2%. IR (KBr, cm^{-1}), 2,958–2,989 (CH_3), 2,831–2,941 (CH_2), 1,751 (C=O), 1,645 (C=N), 1,272 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.25–1.30 (3H, m, C–CH_3), 1.43–1.54 (6H, m, O–C–CH_3), 1.86 (3H, s, N=C–CH_3),1.92 (3H, s, N=C–CH_3), 4.15–4.22 (2H, m, O=C–O–CH_2), 4.71–4.74 (1H, q, $J = 4.0$ Hz O–CH–C=O), 5.13–5.15 (1H, q, $J = 2.1$ Hz, O=C–O–CH–C=O), MS (*m/z*, %): 246 ($(M+1)^+$, 58%), 56 (100%).

*Ethyl 4-[[2-[[(1-methylethylidene)amino]oxy]propionyl]oxy] butanoate (**3f**)*

A light yellow liquid, yield 41.6%. IR (KBr, cm^{-1}), 2,961–2,986 (CH_3), 2,872–2,920 (CH_2), 1,745 (C=O), 1,656 (C=N), 1,181 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.24–1.28 (3H, m, C–CH_3), 1.40–1.46 (3H, m, O–C–CH_3), 1.86 (3H, s, N=C–CH_3), 1.92 (3H, s, N=C–CH_3), 1.95–2.41 (4H, m, O–C–CH_2–C–O, O=C–CH_2), 4.11–4.23 (4H, m, O=C–O–CH_2, O=C–O–CH_2), 4.63–4.64 (1H, d, $J = 7.2$ Hz, O–CH–C=O), MS (*m/z*, %): 260 ($(M+1)^+$, 23%), 115 (70%), 56 (100%).

*Ethyl 2-[[2-[[(1-phenylmethylidene)amino]oxy]acetyl]oxy] acetate (**3g**)*

The reaction solvent was chloroform. A light yellow liquid, yield 40.3%. IR (KBr, cm^{-1}), 3,059 (Ar–H), 1,759 (C=O), 1,611 (C=N), 1,571, 1,491, 1,474 (phenyl), 1,230 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.26–1.29 (3H, q, $J = 2.8$ Hz, C–CH_3), 4.22–4.23 (2H, q, $J = 2.8$ Hz, O=C–O–CH_2), 4.71 (2H, s,

O–CH_2–C=O), 4.84 (2H, s, O=C–O–CH–C=O), 7.36–7.59 (5H, m, ArH), 8.21 (1H, s, Ar–CH=N), MS (*m/z*, %): 266 ($(M+1)^+$, 100%), 104 (50%), 77 (5%).

*Ethyl 2-[[2-[[(1-phenylmethylidene)amino]oxy]acetyl]oxy] propionate (**3h**)*

The reaction solvent was chloroform. A light yellow liquid, yield 45.3%. IR (KBr, cm^{-1}), 3,059 (Ar–H), 1,751 (C=O), 1,603 (C=N), 1,584, 1,489, 1,448 (phenyl), 1,272 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.25–1.28 (3H, m, C–CH_3), 1.52–1.53 (3H, d, $J = 4.0$ Hz, O–C–CH_3), 4.18–4.23 (2H, q, $J = 6.8$ Hz, O=C–O–CH_2), 4.81 (2H, s, O–CH_2–C=O), 5.19–5.21 (1H, q, $J = 2.4$ Hz, O=C–O–CH–C=O), 7.36–7.59 (5H, m, ArH), 8.21 (1H, s, Ar–CH=N), MS (*m/z*, %): 280 ($(M+1)^+$, 100%), 104 (75%), 77(27%).

*Ethyl 4-[[2-[[(1-phenylmethylidene)amino]oxy]acetyl]oxy] butanoate (**3i**)*

The reaction solvent was chloroform. A light yellow liquid, yield 42.7%. IR (KBr, cm^{-1}), 3,059 (Ar–H), 1,732 (C=O), 1,613 (C=N), 1,571, 1,491, 1,447 (phenyl), 1,185 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.22–1.25 (3H, t, $J = 6.0$ Hz, C–CH_3), 1.98–2.02 (2H, m, C–CH_2–C), 2.38–2.40 (2H, t, $J = 5.6$ Hz, O=C–CH_2), 4.10–4.15 (4H, m, CH_2–O–C=O), 4.71 (2H, s, O=C–O–CH_2–C=O), 7.36–7.37 (5H, m, ArH), 8.20 (1H, s, Ar–CH=N), MS (*m/z*, %): 294 ($(M+1)^+$, 5%), 115 (20%), 104 (100%), 77 (13%).

*Ethyl 2-[[2-[[(1-phenylmethylidene)amino]oxy] propionyl]oxy] acetate (**3j**)*

The reaction solvent was chloroform. A light yellow liquid, yield 47.1%. IR (KBr, cm^{-1}), 3,062 (Ar–H),1,754 (C=O), 1,616 (C=N), 1,600, 1,492, 1,448 (phenyl), 1,212 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.25–1.28 (3H, t, $J = 5.2$ Hz, C–CH_3), 1.60–1.62 (3H, d, $J = 8.0$ Hz, O–C–CH_3), 4.19–4.23 (2H, q, $J = 5.2$ Hz, O–CH_2), 4.71–4.77 (1H, q, $J = 8.0$ Hz, O–CH–C=O), 4.95 (2H, s, O–CH_2–C=O), 7.26–7.57 (5H, m, ArH), 8.18 (1H, s, Ar–CH=N), MS (*m/z*, %): 280 ($(M+1)^+$, 25%), 104 (100%), 77 (18%).

*Ethyl 4-[[2-[[(1-phenylmethylidene)amino]oxy] propionyl]oxy] butanoate (**3k**)*

The reaction solvent was chloroform. A light yellow liquid, yield 39.1%. IR (KBr, cm^{-1}), 3,062 (Ar–H), 1,744 (C=O), 1,609 (C=N), 1,596, 1,495, 1,449 (phenyl), 1,272 (C–O–C), ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), δ 1.26–1.30 (3H, t, $J = 8.0$ Hz, C–CH_3), 1.60–1.61 (3H, d, $J = 4.0$ Hz, O–C–CH_3), 1.82–1.83 (3H, d, $J = 4.0$ Hz, O–C–CH_3), 4.19–4.24 (2H, q, $J = 6.6$ Hz, O–CH_2), 4.89–4.92 (1H, q, $J = 4.0$ Hz, O–CH–C=O), 5.17–5.20 (1H, q, $J = 4.0$ Hz, O–CH–C=O), 7.26–7.58 (5H, m, ArH), 8.18 (1H, s, Ar–CH=N), MS (*m/z*, %): 294 ($(M+1)^+$, 40%), 104 (100%), 77 (19%).

Cut carnation flowers preservation test

Fresh, uniform carnation flowers (*Dianthus caryophyllus* L.) were harvested from plants grown under greenhouse conditions. The cut flowers were placed with their cut ends in test solutions. The concentrations of tested compounds were 100 mg/L. The depth of the test solution was 6 cm. The cut carnation flowers were kept in a growth chamber at 25 °C in diffuse light. Each treatment had three cut carnation flowers, every treatment was duplicated five times, and the test solutions were replaced every other day. In the whole test process, the senescence condition of cut carnation flowers was observed and recorded. Full senescence: petals have lost turgidity and the flowers are partially closed, advanced inrolling symptoms and browning.

The data were analyzed by SAS 8.1.

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