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Photoprotectant improves photostability and bioactivity of abscisic acid under UV radiation☆

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ABSTRACT

Photosensitivity causes serious drawback for abscisic acid (ABA) application, but preferable methods to stabilize the compound were not found yet. To select an efficient photoprotectant for the improvement of photostability and bioactivity of ABA when exposed to UV light, we tested the effects of a photostabilizer bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (HS-770) and two UV absorbers 2-hydroxy-4-n-octoxy-benzophenone (UV-531) and 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (BP-4) with or without HS-770 on the photodegradation of ABA. Water soluble UV absorber BP-4 and oil soluble UV absorber UV-531 showed significant photo-stabilizing capability on ABA, possibly due to competitive energy absorption of UVB by the UV absorbers. The two absorbers showed no significant difference. Photostabilizer HS-770 accelerated the photodegradation of ABA and did not improve the photo-stabilizing capability of BP-4, likely due to no absorption in UVB region and salt formation with ABA and BP-4. Approximately 26% more ABA was kept when 280 mg/l ABA aqueous solution was irradiated by UV light for 2 h in the presence of 200 mg/l BP-4. What's more, its left bioactivity on wheat seed (JIMAI 22) germination was greatly kept by BP-4, comparing to that of ABA alone. The 300 times diluent of 280 mg/l ABA plus 200 mg/l BP-4 after 2 h irradiation showed more than 13% inhibition on shoot and root growth of wheat seed than that of ABA diluent alone. We concluded that water soluble UV absorber BP-4 was an efficient agent to keep ABA activity under UV radiation. The results could be used to produce photostable products of ABA compound or other water soluble agrichemicals which are sensitive to UV radiation. The frequencies and amounts of the agrichemicals application could be thereafter reduced.

1. Introduction

Many agrichemicals are sensitive to UV radiation and have very short half-lives, for instance, 6 h for avermectin, and 40 min for phoxim [1]. Thus, application times and amounts of agrichemicals increase to ensure their effectiveness [2]. Abscisic acid (ABA) is an important phytohormone, which promotes seed dormancy by acting as inhibitor [3,4], improves drought resistance by regulating stomatal closure [5,6] and helps whole plant growth by resistance to the abiotic stress [7,8,9]. Exogenous ABA is often used to prolong florescence [10,11,12,13], promote coloring rates of fruit [14,15,16] and improve resistance to drought stress [17,18]. However, ABA exposed to UV radiation is readily losing its bioactivity by isomerizing to *trans*-ABA [19] (Fig. 1), which is proved of much less bioactivity than that of normal ABA [20,21]. And the half-life of ABA is only 24 min [22]. This results in an increasing economic cost for field application of ABA.

Many efforts have been made to keep the bioactivity of ABA and reduce its susceptivity to UV degradation [23,24,25,26]. Chen and Mactaggart [23] replaced the unsaturated carbons in the side chain of ABA to the partial structure of a benzene ring to avoid *cis–trans* isomerization, but the bioactivity of the new compounds were much less than that of ABA. Kim et al. [24] replace the hydrogen in Δ^2 of ABA side chain to fluorine to reduce *cis–trans* isomerization and molecular orbital calculations by GAUSSIAN-90 program using 4-31G basis set showed that the introduction of fluorine at the 2 position indeed stabilized the configuration of the side chain. However, experiments on stability and bioactivity were not found. Wu [25] and Liu [26] changed the double bond in Δ^2 of ABA side chain to cyclopropyl to reduce *cis–trans* isomerization and found significant photostability of the new compound, but the bioactivity was greatly decreased comparing to normal ABA. Up to date, preferable methods were not found yet. Therefore, how to alleviate the photosensitivity of applied ABA is still an unresolved big challenge.

Photoprotectants, mainly UV absorbers and photostabilizers, are agents commonly used in plastic [27], textile [28] and cosmetic products [29] to increase the life of the products and protect human skin from UV damage. It has been well known that only UVB (290 ~ 320 nm) and UVA

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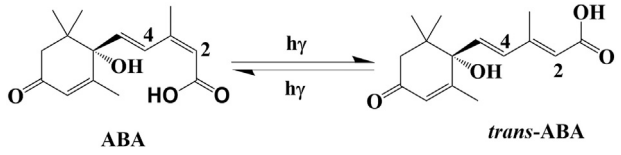


Fig. 1. Structure and photoisomerization of ABA to *trans*-ABA.

(320 ~ 400 nm) radiation in the UV spectrum can pass through the atmosphere and reach the ground. UV absorbers, e.g. UV 531, BP-4, usually have an absorption peak at UV wavelength of 290 nm and 320 nm without affecting the transparency of visible light [30]. The chemical structures of two commercial UV absorbers (UV-531 and BP-4) based on 2-hydroxy-4-methoxybenzophenone are shown in Table 1. The substitute of hydrogen in methoxyl by n-heptane makes UV-531 much harder to solubilize in water while the substitute of hydrogen in the benzene ring by sulfonyl makes BP-4 soluble in water. Both of the two chemicals significantly absorb UVA and UVB radiation without undergoing fast transformation [31,32]. Hindered amines (HS) is highly effective photostabilizer for polymers which are degraded by photooxidation [33]. HS is also used to enhance photo-stabilizing capability of UV absorbers [34]. The chemical structure of a widely used commercial hindered amines (HS-770) is shown in Table 1. The piperidinyl in the structure makes HS-770 show alkaline.

We hypothesized that applying UV absorber and photostabilizer HS could reduce photosensitivity of applied ABA at the field condition and the combination of HS with UV absorber might enhance the efficiency of UV absorbers. The objective of this study was therefore to test the hypothesis, and to compare the effects of oil soluble UV absorber UV-531 and water soluble UV absorber BP-4 with and without photostabilizer HS-770 for the further selection of an efficient photoprotectant. The dynamics of ABA degradation at different doses of selected photoprotectant and bioactivity on plant growth thereafter were also analyzed.

2. Results

2.1. Photodegradation of ABA in the Presence of UV Absorbers

The results indicated a significant improvement of photostability of ABA by applying UV absorbers. ABA, *trans*-ABA concentrations, and especially ratios of *trans*-ABA/ABA in ABA methanol solution after 8 min irradiation were significantly decreased by the addition of UV absorbers BP-4 and UV-531, while ratios of the two UV absorbers were not significantly different from each other (Fig. 2a, b and c). As concentrations of *trans*-ABA plus ABA in the solution almost always equaled to the ones of ABA before irradiation (Fig. 2d), the slopes of the ratios can represent the degradation rate of ABA. The slope of linear regression in the presence of BP-4 or UV-531 was 0.029, which were about 20% lower than that of ABA alone (0.036).

2.2. Effects of HS-770

The results suggested HS-770 not only did not improve the effect of UV absorber, but even worse when it was combined with UV absorber comparing to that of without HS-770. Surprisingly, the treatment of ABA with only adding HS-770 however showed a significant increase of ABA degradation (Fig. 3a, b and c). With HS-770 adding into ABA, the slope of the *trans*-ABA/ABA ratio was 0.041 (Fig. 3c), which was 14% higher than that of ABA alone (0.036). What's more, the slope or saying speed of degradation (min^{-1}), of ABA added with HS-770 plus BP-4 was 10% higher than that of ABA added with BP-4. As concentrations of *trans*-ABA plus ABA in the solution almost always equaled to the ones of ABA before irradiation (Fig. 3d), so the slopes of the ratios also can represent the degradation rate of ABA.

2.3. Degradation Dynamics of ABA Adding with Different Dosages of UV Absorber

Combining application of ABA of 280 mg/l and BP-4 of 200 mg/l in aqueous solution remained 68% effective ABA after 2 h UV irradiation, 56% after 4 h, and 44% after 8 h (Fig. 4). The ABA content after 8 h UV irradiation in adding BP-4 treatment was 1.3 times higher than that of in ABA alone. Intermediate values of remained effective ABA were achieved in adding BP-4 with doses of 50 and 100 mg/l, which two doses showed no significant difference.

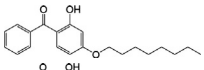
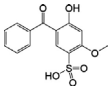
2.4. Remaining Bioactivity of ABA in the Presence of UV Absorber After Irradiation

Shoot and root length of wheat seed were significantly suppressed by the diluents of 280 mg/l ABA alone or the diluents of 280 mg/l ABA plus 200 mg/l BP-4, compared to the treatment of pure water (Fig. 5a and b). Shoot length in ABA plus BP-4 treatment was 13.2% shorter than that of ABA alone, and it was not significantly different with the treatments of un-degraded ABA (Fig. 5a). However, root length instead was significantly longer in degraded ABA treatments than that of un-degraded ones. That probably implied that the root growth was more sensitive to ABA than that of shoot growth. Root length in ABA plus BP-4 treatment was 16.2% shorter than that of in ABA alone (Fig. 5b). Root numbers in treatments of ABA alone and ABA plus BP-4 were significantly less than that of in pure water control, but they did not significantly differ from each other (Fig. 5c). The bioactivity of un-degraded ABA with or without BP-4 showed no significant difference with each other.

3. Discussions and Conclusions

UV absorbers significantly reduced the degradation of ABA under UV light. Two testing UV absorbers UV-531 and BP-4 were found no significant differences with each other. Surprisingly, hindered amines, i.e. HS-770, did not improve the effect of UV absorber. Bioactivity of ABA after irradiation was greatly kept by addition of UV absorber BP-4. Adding

Table 1
The names and configuration of some photoprotectants.

Abbreviation	Chemical name	Configuration
UV-531	2-Hydroxy-4-n-octoxy-benzophenone	
BP-4	2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid	
HS-770	Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate