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Variations in sweet basil in response to Green synthesized Zinc-Amino nano complexes

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ABSTRACT

Since the desires for nanoparticle (NP) applications in agriculture increase, their green and sustainable synthesis has attracted more attention. Zinc nanoparticles are among the most commonly used NPs in agriculture. The present study was planned to determine the variations in sweet basil (*Ocimum basilicum* L.) in response to green synthesized zinc-amino nano complexes. Zinc-glutamine [Zn $(Gln)_2$], zinc-glycine [Zn $(Gly)_2$] and zinc-arginine [$Zn(Arg)_2$] were synthesized via ultrasonic irradiations and their effects were evaluated on vegetative growth, chemical composition and antioxidant activity of sweet basil in comparison to the Zn-EDTA fertilizer. Zinc-arginine produced the biggest amount of vegetative growth and essential oil yield. The predominant component in sweet basil was methyl chavicol. Sweet basil plants that were supplied with $[Zn(Arg)_2]$ had the highest zinc concentration in the shoots. Rosmarinic acid was the predominant phenolic compound in all of the plants that had received treatments. According to the obtained results, the low doses of high effective green synthesized zinc nano-complex could be substituted with the traditional zinc fertilizer to improve the pharmaceutical properties of sweet basil plant.

1. Introduction

The prevalence of nutritional deficiency in soils can result in economic loss for farmers. It can also reduce the quality of produce and can lower the overall yield of crops. Large scale applications of chemical fertilizers not only disturb the soil mineral balance but also reduce soil fertility. Nano-complexes can enhance crop productivity by increasing the photosynthetic activity, the rate of seed germination, seedling growth, metabolism of the nitrogen, carbohydrate and protein synthesis. Other benefits of these nano-complexes may include increased stability/solubility, slow release, increased uptake or translocation and, in some cases, targeted delivery. The availability of nutrients is the most important manageable factor which plays a considerable role in the biosynthesis, yield and quality of essential oils and phenolic compounds that are often derived from plants (Chand et al., 2015; Pal et al., 2016). Chemical components and the yield of essential oils correlate with the amounts of nutrients that are available to plants (Hanif et al., 2017). Plant nutrients regulate several physiological activities in crops (Yadegari, 2014). Previous studies have shown that fertilizers commonly affect the main components of *Pimpinella anisum* and *Satureja hortensis* essential oils (Tavallali et al., 2017a; Alizadeh et al., 2010). Zn is an essential micronutrient for plants to exhibit normal growth and plays vital roles in the biosynthesis of terpenes, the accumulation of saccharides, free radical scavenging, carbon assimilation and antioxidant enzymes (Rezaeieh et al., 2016). When plants are deficient in Zn, the essential oil yield and vegetative growth of plants can be adversely affected (Ali et al., 2008). Natural and synthetic zinc fertilizers are used extensively to prevent Zn deficiency in soils and the most popular forms are chelates, i.e. Zn-DTPA, Zn-EDTA and Zinc-sulfate (Cakmak et al., 1999; Welch, 2002; Khoshgoftarmanesh et al., 2010; Alloway, 2004; Ghasemi et al., 2013; Vadas et al., 2007). However, synthetic chelates often carry several disadvantages. They can cause toxicity for plants and may disturb the micronutrient balance in the soil. When other positively charged ions, such as calcium and magnesium, are present in high concentrations, they compete with the Zn ion for binding to the ligand. The Zn ion might then be replaced, making the chelate ineffective in delivering the Zn ion to the plant (Mohammadi and Khoshgoftarmanesh, 2014). Applying nanostructure compounds in plants is one of the most significant branches of nanoscience.

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Supplying nutrients by using nano-complexes is a unique and novel approach that is related to the large numbers of surface molecules (Kim et al., 2004). Nano-fertilizers may decrease environmental risks and soil pollution that happen when using chemical fertilizers (Davarpanah et al., 2016). Application of nano-fertilizers in smaller amounts than common fertilizers is the main advantage of their using (Subramanian et al., 2015). The nano Zn characteristics such as reactivity, specific surface area and size affect the Zn solubility and availability to plants. Nano zinc chelates with these specifications can be designed as a new fertilizer (Mosanna and Khalilvand, 2015). Positive effects of the foliar application of zinc nano chelated fertilizer were demonstrated on essential oil content and zinc concentration of *Satureja hortensis* (Najafivafa et al., 2015). We also reported the positive effects of zinc-amino levulinic acid nano-complex on bioactive compounds of *pimpinella anisum* (Tavallali et al., 2017b).

Zinc-amino acid chelates are an advanced alternative to the classical methods of overcoming Zn deficiency (Aravind and Prasad, 2005; Ghasemi et al., 2013). Basil (*Ocimum basilicum* L.) is grown around the world and is commonly used as a food flavoring agent. It has applicability in the realm of essential oils and can be used in traditional medicinal practices. Basil is a key ingredient in vinegars, oils, cheese, jams, teas, drinks and liqueurs. It has an extensive list of traditional medicinal uses. The unique health benefits of basil are primarily due to its essential oil contents (Singh et al., 2014; Farouk et al., 2016; Bilal et al., 2012; Beatovic et al., 2015; Hanif et al., 2017; Vieira et al., 2014; Hussain et al., 2008; Sajjadi, 2006; Abad et al., 2012).

The present study is the first of its kind to evaluate the effects of zinc-amino acid nano chelates (n [Zn $(Gln)_2$], n [Zn$(Arg)_2$] and n [Zn $(Gly)_2$]) on the chemical composition and antioxidant activity of sweet basil's essential oil.

2. Materials and methods

2.1. Preparation and characterization of nano sized Zn-amino acids complexes

Nano sized Zn-amino complexes were prepared by dissolving 2 mmol of amino acid (Glutamine (Gln), Glycine (Gly) and Arginine (Arg)) in 5 mL of deionized distilled water. Then, this solution was mixed with a solution of Zn $(AOc)_2$ (1 mmol) in 2 mL distilled water by sonication via an ultrasonic probe (Oscillation of 90% for 30 min). The mixtures were dried under vacuum for 18 h to obtain a dry dark brown powder. The features of nano particles were characterized via the transmission electron micrographs (TEM) (100 kV Philips, EM208), EDX (Tescan Vega II, with a Rontec detector) and FTIR (Tensor II FTIR spectrometer).

2.2. Plant culture

A greenhouse trial was considered at the Shiraz Payame Noor University situated in Golestan town (29° 36′ N and 52° 32′ E, 1490 m above sea level). The soil was a fine topsoil loam (taken from 0 to 30 cm of virgin soil) which were characterized by (Alloway, 2004) pH (7.1), ECe (1.2 dS m^{-1}), CEC (10 Cmc kg^{-1}), organic (8.9 g kg^{-1}), N (0.07%), P (13 mg kg^{-1}), K (59 mg kg^{-1}) and DTPA-extractable Fe (2.21 mg kg $soil^{-1}$) and DTPA-extractable soil Zn (0.5 mg kg^{-1}). The N and P were applied to the soil at a concentration of 50 mg kg^{-1} soil, while the Cu, Fe and Mn were applied at a concentration of 5 mg kg^{-1} soil. In a uniform manner, they were given to the soil as NH_4NO_3, KH_2PO_4, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$ and $MnSO_4.H_2O$, respectively. Plastic pots that measured 8 L in volume were used, and 7.5 kg of soil was considered for each pot. Twenty certified seeds of sweet basil (*Ocimum basilicum* L.) which were obtained from a herbalist's shop (Shiraz, Iran) were planted in each pot and were irrigated with deionized water twice weekly to maintain the soil at field capacity. After fifteen days, the plants were thinned to 10 uniform stands in each pot. After thinning and before the onset of flowering, Zn was sprayed at a concentration of 0.2% (w/v) in the forms of synthetic Zn-Glutamine [Zn $(Gln)_2$], Zn-Glycine [Zn $(Gly)_2$] and Zn-Arginine [Zn$(Arg)_2$] nano complexes and Zn-EDTA. Each treatment contained eight pots (replication) including 10 seedlings in each one. In each treatment, 1 L of each chelate solution at the rate of 0.2% (w/v) zinc was sprayed. Deionized water was also sprayed as the control group. During one week, plants were harvested at full bloom stage and were then positioned in the shade at room temperature (20–25 °C) for 4 days.

2.3. Plant extracts preparation

The dried plant material was ground into powder by using a hand mill. Twenty grams of dried *Ocimum basilicum* L. samples were extracted in 250 mL of methanol/water (90:10 v/v) for about 24 h at room temperature (20–25 °C) and then filtered through membrane filters with pore sizes measuring 0.22 μm in diameter for injecting HPLC for polyphenolic determination (Najafian and Zahedifar, 2015). The residue was then dried by a rotary evaporator for antioxidant activity analysis.

2.3.1. Antioxidant activity

Antioxidant activity was assessed based on free radical DPPH scavenging potential of sweet basil (Burits et al., 2001). Accordingly, 25 μL of 12–3100 μg mL^{-1} gallic acid or methanolic extracts were blended with 220 μL of 120 mmol L^{-1} radical solution of DPPH in methanol for 30 min at ambient temperature. Absorbance of solutions was measured at 515 nm wavelength using an EL×808 absorbance microplate reader (BioTek Instruments Inc., USA). The IC_{50} values of samples (which is the concentration (mg L^{-1}) needed to restrain DPPH radical formation by fifty percent) were determined by the nonlinear regression plots using MATLAB (The MathWorks Inc., USA). The following equation was used in order to determine the antioxidant activity:

$$\text{Antioxidant activity} = 1 - [(A_{sample} - A_{blank})/A_{control}] \times 100$$

Where A_{sample} and A_{blank} are absorption values of the test solution (t = 30 min) and the blank solution (t = 0 min). DPPH (without plant extract) and methanol were utilized as control and blank, separately.

2.4. Preparation of essential oil (EO)

The plants were shaded at room temperature (20–25 °C). The EO of all dried samples (100 g) was isolated by hydrodistillation for 3 h, using a Clevenger-type apparatus according to the method recommended in the British Pharmacopoeia (British pharmacopoeia., 1988). The oil sample was dried over anhydrous sodium sulfate and was kept at 4–8 °C until the analysis was performed.

2.5. Oil analysis procedure

Analyses of the volatile extracts were carried out by gas chromatography (GC) and by gas chromatography-mass spectrometry (GC-MS). Analytical GC was carried out in a gas chromatograph (Agilent, Model 7890A,G3440A), equipped with a flame ionization detector (FID), an autosampler (Agilent, Model 7683B), Agilent HP-5 fused silica column (5% phenylmethylpolysiloxane), 30 m × 0.32 mm i.d., film thickness 0.25 μm, and an Agilent