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RESEARCH ARTICLE

Effects of molybdenum on nutrition, quality, and flavour compounds of strawberry (*Fragaria*×*ananassa* Duch. *cv*. Akihime) fruit

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Abstract

Molybdenum (Mo) is an essential trace element in plant nutrition and physiology. It affects photosynthesis and photosynthate accumulation, therefore also affecting fruit quality and nutritional content. This study assessed the effects of different sodium molybdate (Na_2MoO_4) concentrations on strawberry. Five different Mo concentrations were applied in this experiment, including 0, 67.5, 135, 168.75, 202.5 g ha^{-1}, respectively. The mineral concentration, including nitrogen (N), Mo, iron (Fe), copper (Cu), and selenium (Se) was assessed in strawberry fruit, as well as chlorophyll content, nutrition quality, taste and aroma. Results showed that net photosynthetic rate (P_n) and chlorophyll content for the strawberry plants increased with an increase in Mo concentration; and the contents of N, Mo, Fe, Cu, total soluble solids (TSS), titratable acidity (TA), sweetness, some sugars, organic acids, and some volatile compounds in the fruit all increased, as well. However, the Mo concentration did not significantly affect the concentrations of Se, sucrose, lactic acid, acetic acid, and some aroma compounds. Fruit sprayed with 135 g ha^{-1} Mo exhibited the highest TSS and sweetness values, as well as the highest N and Fe concentrations among all the treatments. P_n value and chlorophyll content, fructose, glucose, sorbitol and total sugar contents in fruit supplied with 135 g ha^{-1} Mo were also higher than that in other treatments. Fruit sprayed with a Mo concentration of 67.5 g ha^{-1} exhibited significantly higher ascorbic acid (AsA) values than that of control. Ninety-seven volatile compounds were identified in fruit extracted by head-space solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS). Fruits sprayed with 135 g ha^{-1} Mo had the highest concentrations of six characteristic aroma compounds, including methyl butanoate, γ-decalactone, ethyl butanoate, methyl hexanoate, γ-dodecalactone, and ethyl caproate.

Keywords: strawberry, molybdenum, nutrition, volatile compounds, flavour

1. Introduction

Compared to other micronutrients, molybdenum (Mo) is the least available nutrient to plants in acid soil conditions (Marschner 1995). Mo easily binds with free iron (Fe) and aluminum when the soil pH value is <5.5 (Gong *et al.* 1998). In China, excessive or inappropriate fertilizer application leads to acidification of orchard soil (pH<5.5), thereby decreasing Mo availability. The phenotype of Mo-deficient plants is characterized by altered morphology of leaves, impaired

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flower formation, poor fruit quality, and an overall stunting in plant growth. Foliar application of Mo is an effective means of improving Mo deficiency of plants. Previous studies found that Mo foliar sprays on Merlot grapevines increased yield and berry size (Longbottom *et al.* 2010). Eshghi *et al.* (2010) reported Mo increased pollen germination rate of strawberry. However, to our knowledge, little research has been conducted on the role of Mo on strawberry fruit quality.

Mo is a trace element for plant growth. Once molybdate enters the cell, it is subsequently incorporated by complex biosynthetic machinery into Mo co-factors (Moco). Moco, as a prosthetic group, participates in the active site of Mo enzymes, such as nitrate reductase, xanthine dehydrogenase, aldehyde oxidase, sulphite oxidase, and the mitochondrial amidoxime reducing component. These enzymes play an important role in nitrate assimilation, phytohormone biosynthesis, purine metabolism, sulfite detoxification, and the reduction of a broad range of N-hydroxylated compounds (Hille *et al.* 2011). Mo is involved in nitrogen (N) metabolism of plants (Kaiser *et al.* 2005). Mo deficiency prevented the transformation from δ-aminolaevulinic acid to uroporphyrinogen III, and thus inhibited the biosynthesis of chlorophyll, resulting in a decrease in chlorophyll in winter wheat cultivars (Yu *et al.* 2006). The biosynthesis of flavour compounds is dependent on the primary and secondary metabolites derived from photosynthesis (Carrari and Fernie 2006). Enhanced chloroplast development and chlorophyll content increases leaf and fruit photosynthetic capacity, which provides more substrate for precursors of sugars, organic acids, and volatile aroma compounds (Nadakuduti *et al.* 2014).

Increased demand for high-quality fruit with unique colour, high nutritional value, and good flavour has lead to a proliferation in research on fresh fruit quality, including physicochemical and flavour characteristics. Strawberry flavour is derived from a combination of its taste and aroma. The taste of strawberry primarily depends on sugars and organic acids, whereas its aroma depends on numerous volatiles. Over 360 volatile compounds have thus far been reported in ripe strawberry (Raab *et al.* 2006), including esters, organic acids, alcohols, ketones, phenols, terpenes, furanones, aldehydes, lactones, sulfur compounds, and epoxides. Mineral elements are also key factors in strawberry fruit quality. However, while the effect of N (Ancín-Azpilicueta *et al.* 2013), calcium (Holb *et al.* 2012), carbon dioxide (Xi *et al.* 2014), phosphorus and potassium (Topalović *et al.* 2011) on fruit quality have been described, the effects of Mo fertilizer application on flavour and nutritional quality have not been reported.

In this context, we evaluated the effect of Mo on strawberry fruit quality, mineral element content, net photosynthetic rate (P_n), chlorophyll content, total soluble solids (TSS), titratable acidity (TA), TSS/TA, composition of sugars and acids, and volatile compounds in strawberry under different Mo treatments.

2. Materials and methods

2.1. Plant propagation and growth

Strawberry (*Fragaria×ananassa* Duch. *cv*. Akihime) seedlings (*n*=200) were grown in a soilless system with elevated horizontal troughs filled with coir substrate. Seedlings were irrigated with modified Hoagland's nutrient solution (Hoagland and Arnon 1950) without Mo. Plants were treated with foliar sodium molybdate (Na_2MoO_4) at four different doses (67.5, 135, 168.75, 202.5 g ha^{-1}), and plants sprayed with ultrapure water served as the control. The Mo concentrations described in the paper were selected from previous experiments as shown in the Appendix A. The Mo concentration of 168.75 g ha^{-1} produced the healthiest plants. Plants sprayed with Mo concentrations of 675 and 1 350 g ha^{-1} showed symptoms of poisoning. The Na_2MoO_4 treatment was applied at intervals of 7 d from October 20, 2014 to January 31, 2015. All solutions were prepared with deionized water. The experiments were conducted under natural light (25–28°C in the daytime and 5–10°C at night), and at 55–65% relative humidity in the greenhouse at Shandong Agricultural University, China. At full maturity, at least 90 fruits for each treatment were harvested in the same experimental plantations, filled with polystyrene punnets and carried to the laboratory at 4°C. The strawberry samples used for fruit quality analysis were divided into three groups. The samples representing class I, consisting of 30 fully-ripe, red fruit (10 fruit per replicate) from each treatment, were used for testing volatile compounds, sugars, and organic acids. Thirty representative fruit (10 per replicate) from class II were stored at 4°C in the dark, overnight for the simultaneous analysis of TA and TSS. Thirty more fruit (10 per replicate), representing class III, were dried to test for mineral elements (Mo, Fe, copper (Cu), selenium (Se)).

2.2. Determination of mineral elements using inductively coupled plasma mass spectrometry (ICP-MS)

Trace minerals (Mo, Cu, Fe and Se) were determined by the NexION™ 300 ICP-MS System (Perkin Elmer, USA) consisting of a bench-top ICP-MS instrument, roughing pump, re-circulator, data acquisition and analysis software, equipped with a low liquid uptake nebulizer, a free-running radio frequency (RF) plasma generator, automated X, Y, Z torch positioning, and a four-stage vacuum system. A MARS6 (CEM, USA) high-throughput closed microwave digestion workstation was used for dissolving metals and