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Special Research Report # 464: *Post Production*

Inhibitors of Ethylene Action for Improving Cut Flower Longevity

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BACKGROUND

Ethylene is a gaseous molecule produced in various parts of higher plants. It acts as a plant hormone causing several adverse effects such as fading and wilting of flowers, accelerated bud, petal, and leaf drop, yellowing of leaves and premature shattering of flowers. Currently, 1-methylcyclopropene (1-MCP) treatment has been utilized to block the ethylene effect on and enhance the longevity and quality of floriculture crops. Silver thiosulfate (STS) treatment is also effective. However, both these options have their own drawbacks. For example, gaseous 1-MCP is quite reactive and difficult to handle and requires enclosed areas for application. There are environmental concerns and disposal challenges of using heavy metal containing STS, especially in large quantities. The objectives of this research are to get a deeper understanding of plant-ethylene chemistry and to find better inhibitors of ethylene action. In particular, we plan to (i) develop user friendly chemicals to stop the adverse ethylene effects on plant tissue that can be utilized in cut flower industry and on floricultural crops, (ii) prepare easily isolable, simple laboratory models of ethylene binding site in plants to facilitate the testing of potential alternatives to 1-MCP more conveniently, and (iii) investigate the mode of action of 1-MCP on ethylene binding sites.

MATERIALS AND METHODS

Several, water soluble 1-MCP analogs with various polar substituents have been prepared as potential ethylene antagonists. In addition, reactive carbon centered molecules with the potential to react strongly with copper (which is the ethylene binding center in plants) have also been prepared and isolated. Simple molecular models of

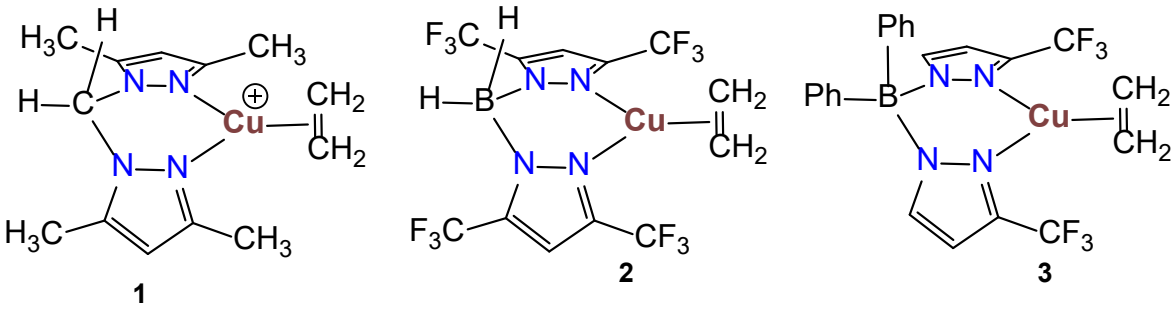
ethylene binding site (synthetic ETR1 models) were assembled using copper ions, ethylene and nitrogen-based chelators. New molecules have been characterized using nuclear magnetic resonance and infra-red spectroscopy, X-ray crystallography and other modern analytical techniques. The anti-ethylene activities of 1-MCP alternatives were tested using fresh carnations with the help of a collaborator active in floriculture research. The reactivity of ethylene antagonists towards synthetic ETR1 models was also investigated to observe the nature of interaction.

RESULTS

User friendly alternatives to 1-MCP: We have synthesized several non-volatile cyclopropenes (1-MCP alternatives) and tested their anti-ethylene activity using fresh carnations. Some of them also shows good water solubility. They are much more convenient to use compared to the more reactive and gaseous 1-MCP. Two of the tested cyclopropenes displayed reasonable activity. In addition, a reactive carbon centered reagent (which is not a cyclopropene) displayed very strong anti-ethylene activity based on the tests done on cut flowers. We are excited about this finding as it is different from 1-MCP chemistry and provides a different approach to designing ethylene antagonists. We plan to develop new and improved anti-ethylene reagents by modifying the structural features of promising ethylene antagonists uncovered during this study.

Synthetic models of ethylene binding site in plants: Four isolable molecules that feature copper(I)-ethylene bonds (copper-ethylene complexes) have been synthesized and isolated successfully. Three examples are illustrated as **1-3** below (Figure 1). We believe that these molecules can serve as laboratory models for the copper-ethylene binding site in plants. Silver-ethylene complexes of **1** and **3** have also been isolated. They bind ethylene relatively weakly compared to the copper complexes. Since acetylene can also cause ethylene like effects, interaction of acetylene with copper sites (e.g., in **1-3**) was also probed. The data suggest that acetylene binds to copper sites more strongly and can displace ethylene on copper.

Figure 1



Molecules with copper-cyclopropene bonds: The widely used 1-MCP is a reactive organic molecule with a three-carbon ring. It is a cyclopropene and known to interact strongly with the ethylene binding sites in plants, which has copper centers. However, very little is known about the exact nature of this interaction. During this project period, we for the first time, managed to isolate molecules that show copper-cyclopropene bonds. The X-ray crystallographic data have been used to confirm the presence of 1-MCP like species (cyclopropene) on copper. Molecular structures of two of those are illustrated in Figure 2.

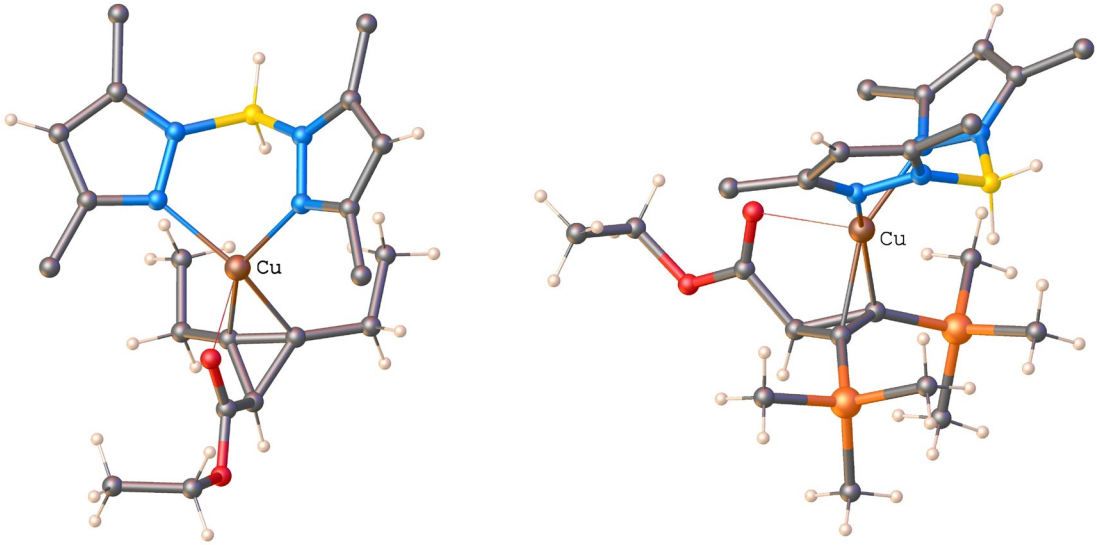


Figure 2. Two molecular structures that show copper atoms interacting with cyclopropenes (1-MCP analogs)

Some of the discoveries noted above have been reported in two high-quality research publications.

Isolable acetylene complexes of copper and silver; Noonikara-Poyil, Anurag; Ridlen, Shawn G.; Fernandez, Israel; Dias, H. V. Rasika, *Chemical Science* (2022), 13(24), 7190-7203.
Isolable Copper(I) η^2-Cyclopropene Complexes; Noonikara-Poyil, Anurag; Ridlen, Shawn G.; Dias, H. V. Rasika, *Inorganic Chemistry* (2020), 59(24), 17860-17865.

CONCLUSIONS

We have uncovered some non-volatile 1-MCP alternatives with good anti-ethylene activity. One of these based on a reactive carbon centered molecule is very different from 1-MCP and represents a new class of compounds with impressive activity. Four novel, chelating nitrogen-donor supported, copper-ethylene compounds that can act as an ETR1 models have also been synthesized and isolated. They have copper-ethylene bonds and have been utilized to test the activity of 1-MCP alternatives on copper and affinity of

acetylene towards ethylene binding sites. We, for the first time, have uncovered and completely characterized several copper-cyclopropene complexes. They show the mode of likely interaction between the ethylene-binding sites of plant and 1-MCP.

INDUSTRY IMPACT

- The identified 1-MCP alternatives have the potential to be formulated into products for controlling the adverse effects of ethylene in floriculture crop products.
- Synthetic "ethylene binding site" models speed up the screening of new anti-ethylene products.
- Structures of molecules that provide insights to the 1-MCP action in plants are useful for developing better and more effective anti-ethylene reagents.

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