

Abstract

Superficial scald is an oxidative postharvest storage disorder of apple fruit, characterized by necrosis of the first 5-6 hypodermal cell layers that can leave the fruit unmarketable. The antioxidant diphenylamine (DPA) has been used as a primary means of scald control for apples. The scald control mechanism of DPA is unknown. These studies examined DPA derivative formation during and following storage as well as in conjunction with fruit treatments that are known to affect scald. The mechanism of scald control by DPA was also investigated by treating fruit with DPA and DPA derivatives and then monitoring scald formation and derivatization of the treatment compounds.

Compounds identified and routinely quantified included DPA, 4-hydroxydiphenylamine, 3-hydroxydiphenylamine, *N*-nitrosodiphenylamine, 4-methoxydiphenylamine, 3-methoxydiphenylamine, 9 *H*-carbazole, 4-nitrodiphenylamine, and 2-nitrodiphenylamine. Derivatives substituted in the *para* position offered varying degrees of scald control, depending on the chemical nature of the functional group, while those substituted in the *ortho* and *meta* positions provided no control. *C*-Hydroxylation of treatment compounds had little relationship to DPA mediated scald control. Partial control was provided by *N*-nitrosodiphenylamine due to its prevalent degradation to DPA indicating that an empty amino position is crucial for scald control. Peel content of *N*-nitrosodiphenylamine, 2-nitrodiphenylamine, and 4-methoxydiphenylamine were reduced by ethylene insensitivity and increased with post-storage ripening in some instances indicating a relationship between their presence and ripening. 4-Methoxydiphenylamine and 3-methoxydiphenylamine presence resulted from *O*-methylation rather than *C*-methoxylation. 4-Hydroxydiphenylamine content and DPA absorption were affected by at-harvest maturity. Hypoxic storage reduced *N*-nitrosodiphenylamine content but had no consistent affect on other derivative formation.

Derivative formation may reflect interplay between reactive oxygen and nitrogen species or other reactions. Definite associations between scald incidence and derivative presence were not readily apparent. These results indicate that DPA derivative formation is not the principle mechanism of scald control by DPA as it is with gunpowder stabilization but, instead, donation of the amino hydrogen to quench radical cascades and resonance stabilization of the diphenylamidogen radical may play an important role.