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Sulfoglucosides as Novel Forms of Modified Mycotoxins

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Being ubiquitous in nature, *Alternaria* species are often found in food and feed. Several *Alternaria* strains produce toxic secondary metabolites, including Alternariol (AOH) and Alternariol monomethyl ether (AME). Both are frequently detected in various vegetables, fruits, and grains. Although their acute toxicity is not very high, they exhibit genotoxicity *in vitro* by inducing gene mutations and DNA strand breaks, and by inhibition of topoisomerases I and IIα. Due to their potential harmful effects, AOH and AME are a public health concern.
Fungi infested plants are able to protect themselves against mycotoxins by altering their chemical structures. A recent study demonstrated that AOH and AME were glucosylated and partially associated with malonate in plant cell suspensions [1]. To evaluate the relevance of these "modified" mycotoxins in food products, tomatoes were infected with spores of cultures of *Alternaria alternata*. Following incubation, however, only trace amounts of glucosylated conjugates were found. Instead, mainly sulfate-conjugates were detected. From this study it was not possible to deduce whether these modifications are caused by the plant or by the fungi itself. Therefore, tomato tissues were individually incubated with cultures of *A. alternata* or the mycotoxins AOH and AME, respectively. In the absence of the fungus, glucosides were formed without detectable amounts of sulfate conjugates. Incorporation of the fungus in the experiment demonstrated that the sulfate conjugates are fungal metabolites.
Incubation of isolated sulfate conjugates in tobacco cell suspension and tomato ex-plant cultures showed the formation of three sulfoglucosides of AOH and one sulfoglucoside of AME. NMR-spectroscopic analysis unambiguously determined the structures of two AOH conjugates and the AME conjugate as alternariol-3-sulfate-9-glucoside, alternariol-9-sulfate-3-glucoside, and alternariol-9-O-methyl ether-3-sulfate-7-glucoside. The third AOH sulfoglucoside was not isolated in sufficient amounts and purity for NMR spectroscopy, but is assumed to arise from the predominant sulfate conjugate alternariol-9-sulfate through glucosylation at C-7. Subsequently, these metabolites were also found in tomatoes infested with *A. alternata*.
These mixed sulfate/glucoside diconjugates are newly described forms of modified mycotoxins, which may also be formed of other mycotoxins and/or their phase I metabolites carrying two or more hydroxyl groups.

Literatur

[1] Hildebrand AA, Kohn BN, Pfeiffer E, Wefers D, Metzler M, Bunzel M. Conjugation of the mycotoxins alternariol and alternariol monomethyl ether in tobacco suspension cells. Journal of Agricultural and Food Chemistry 2015; 63(19): 4728–4736.