

**POLYSUBSTITUTED BENZENES AS DEFENSE COMPOUNDS OF THE
SPRINGTAIL *CERATOPHYSELLA DENTICULATA***

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Collembola are soil-inhabiting arthropods and closely related to the Insecta, from which they diverged about 400 mya. It is assumed that Collembola, similarly to insects, use semiochemicals for communication and defensive purposes. However, our understanding of the collembolan chemistry is limited. The primary defense mechanism of Collembola, or springtails, is their ability to catapult themselves out of danger using their furca, a tail-like appendage. However, soil-dwelling or soil-inhabiting species have a reduced or absent furca and rely more on chemical defenses for protection. To learn more about the chemical defenses of *Ceratophysella denticulata*, we utilized a combination of GC/MS and GC/IR, supplemented by synthesis. This approach allowed us to elucidate the structure of a group of novel, highly substituted benzenes. Total synthesis confirmed the proposed structure and enabled us to perform bioactivity assays. These demonstrated a deterrent effect on predatory insects. Although highly hetero-atom substituted benzenes have been reported as natural products in bacteria and marine invertebrates, there have been no previous reports in insects and other arthropods, to our knowledge. The high abundance of these compounds in *C. denticulata* indicates their importance for the springtail. We have identified earlier 4-methoxy-5-(methylthio)benzo[d][1,3]dioxole, 5-ethyl-7-methoxy-6-(methylthio)benzo[d][1,3]oxathiole, and 5,6,7-trimethoxybenzo[d][1,3]oxathiol-4-amine, the latter being the first fully hetero-substituted benzene from nature.

A further, a more detailed analysis of the Collembola contents revealed three additional benzenes. The structure was deduced from HR-MS data, because the concentration was too low for GC/IR analysis. Therefore, a trial-and-error synthetic approach was used. This approach led to the identification of benzo[1,2-d:4,5-d']bis([1,3]dioxole), the obvious precursor benzo[d][1,3]dioxole-5,6-diol, and 7-methoxy-6-(methylthio)benzo[d][1,3]dioxol-4-amine. In summary, the defense system of *C. denticulata* uses a diverse array of benzenes. Whether they also play a role in intraspecies communication, as has been shown for 1,3-dimethoxybenzene, remains unclear.

Keywords: Substituted benzenes, Collembola, defense, synthesis, mass spectrometry

