Gembloux Agro-Bio Tech
Université de Liège

Le Corps professoral de

Gembloux Agro-Bio Tech - Université de Liège vous prie

de lui faire l'honneur d'assister à la défense publique de la dissertation originale que

Madame DETHIER Bérénice,

Titulaire d'un master bioingénieur chimie et bio-industries, à finalité spécialisée

présentera en vue de l'obtention du grade et du diplôme de

DOCTEUR EN SCIENCES AGRONOMIQUES ET INGENIERIE BIOLOGIQUE,

le 17 août 2016, à 14 heures, en l'auditorium de Chimie Analytique**,**

Passage des Déportés, 2 à 5030 **GEMBLOUX.**

Cette dissertation originale a pour titre :

« The chemistry of new garlic-derived organosulfur compounds and the molecular basis of olfaction »

Le jury est composé comme suit :

Président : Prof. D. PORTETELLE, Vice-Président du Département AgroBioChem,
Membres : Prof. M-L FAUCONNIER (Promoteur), E. BLOCK (Copromoteur, Albany, USA), G. LOGNAY, M. FREDERICH, A. RICHEL, S. LANNERS (Unamur).

Abstract

Garlic is a very popular condiment that has been used around the world for centuries. It is also a source of a remarkably extensive range of organosulfur compounds, whose chemistry is the focus of this thesis. The central reaction in formation of these compounds is the enzymatic cleavage of alk(en)yl cysteine sulfoxides by alliinases, which leads to sulfenic acids. The latter can then undergo condensation and rearrangement into various organosulfur compounds. Three aspects of the chemistry of garlic have been investigated in this thesis.

First, little studied, minor organosulfur compounds in extracts of freshly chopped garlic were studied. These higher molecular weight compounds (MW 150 – 550) can be conveniently studied using state-of-the-art LC-MS and DART-MS techniques. Novel garlic-derived compounds were studied and the structure of one representative compound containing a five-membered thiolane ring, ajothiolane, was determined by spectroscopic methods, using synthetic analogues as spectroscopic standards. The fate of compounds in a garlic extracts over time was also studied, since the new, higher mass sulfur compounds are slowly formed by rearrangement of smaller metabolites a few days after maceration of the garlic.

A second part of this thesis provides hands-on methods for the analysis and preparation of key garlic metabolites. The isolation and/or synthesis of alliin, alliinase and vinyldithiins have been optimized, and are proposed as turnkey procedures for future work.

Finally, in an effort to explain the unique odor of garlic-related thiols and sulfides (in garlic breath, sweat, etc.), the interactions between odorants and olfactory receptors have been studied. Work described in this thesis contributed to this larger project by designing and synthesizing model macrocyclic odorants to resolve the mechanism of olfaction at the receptor level. The conclusions, arguing against the plausibility of the so-called “vibrational theory of olfaction”, have been published as a foundation for future work on olfactory detection of thiols and other sulfur-containing compounds.