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Green waste valorization: Microwave-assisted modifications of the hemolytic and antifungal saponins contained in *Aesculus hippocastanum* seed

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Saponins are natural amphiphilic molecules that are found in some marine animals, e.g., sea cucumbers or sea stars, but abundantly in the plant kingdom. These molecules are specialized metabolites and are reputed to be essential for the relationships between plants/animals and their ecosystem since they intervene in the communication and defense processes. For decades, their surfactant properties have been valorized as soaps and detergents and their cytotoxicity presents great avenues in cosmetic, pharmaceutical, and medical research [1]. Part of our recent research focuses on the valorization of biomasses with a special interest in the development of biointrants in the context of biological agriculture. In the present study on horse chestnut saponins, we report on the mass spectrometry identification and the targeted chemical modifications of these specialized metabolites. We further evaluated the biological activities, i.e., cytotoxicity and antifungal properties, of the (modified) saponins in the context of defining the structure/activity relationship and proposing high-added value applications of this green waste. The horse chestnut is one of the most abundant ornamental trees in Europe. Chestnut seeds are nevertheless discarded due to the presence of toxic compounds, such as esculin and saponins. These saponins, the so-called Escins, are monodesmosidic saponins based on a(n) sapogenin/aglycone (apolar part) substituted in different positions by different acyl chains. The glycan (polar part) is always a branched trisaccharide. The first step of the project consisted of the structural characterization of the seed-extracted saponins by mass spectrometry techniques. The identification and quantification of saponins were carried out by MALDI-ToF and LC-MSMS experiments. Nine compositions have been identified, for a total of twenty-four isomers. Flash chromatography was further used to generate an Escins I, II and III enriched-extract. Secondly, since the isolated Escins present two ester groups on their aglycones (tigloyl/angloyl group on C21, and acetyl group on C22 or C28), we selectively hydrolyzed these ester groups upon microwave activation. During our optimization, we detected new saponins in which the acetyl group is displaced from C22 to C16. Finally, we evaluated the impact of the chemical modifications on the cytotoxicity of the saponins based on a hemolytic activity assay and the antifungal activities of the (modified) saponins against *Alternaria solani*, a fungal pathogen of tomato and potato crops, have also been shown to be tuned by the chemical modifications.

References

1. P. Savarino et al.; Mass Spec Rev., 1-30 (2021)