



Selective synthesis of polyols from renewable resources

Synthèse sélective de polyols à partir de matières premières renouvelables

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<u>Context</u>: Insects interact extensively with their environment through small molecules. This area of research is commonly referred to as 'chemical ecology' and is one of the few alternatives to the use of insecticides, which are effective but cause serious environmental problems. In general, these molecules are species-specific and induce either repulsion (allowing the protection of exposed populations, plants or animals) or attraction (allowing the creation of selective traps). This is a very important area of research for France, which has seen an increase in the population of disease-carrying mosquitoes in recent years.

<u>State of the art:</u> There are many synthetic repellents, some of which are very effective but have their drawbacks. The most effective is DEET, which is still widely used but has an unpleasant odor and is known to be neurotoxic in high doses. Only PMD, a natural product (dihydroxyparamenthane), has sufficient repellent activity to be used, although it is much weaker than synthetic repellents. In addition, although it is present in certain essential oils (Eucalyptus citriodora), this product is obtained by hemi-synthesis from citronellal isomers, which are natural but expensive products. There is a clear need for new natural repellents or repellents of natural origin with an activity equal to or greater than PMD, which are low cost and can be used as a 'cocktail' of natural products.

Project: In this context, we are interested in the modification of terpene derivatives into dioxygenated products (diols, hydroxyketones, diketones). In particular, dihydroxy-limonene were prepared by treatment with potassium permanganate. These conditions led to the formation of 4 compounds which could be separated by chromatography. Their repellent properties were evaluated. Many of these compounds have significant repellent properties against mosquitos.



The interest in this discovery is linked to the possibility of producing effective and inexpensive repellents of natural origin, as well as the possibility of producing formulations combining two or more natural repellents. The synthetic routes explored so far give low yields and produce stoichiometric amounts of waste.

As a consequence, the aim is to propose alternatives using more environmentally friendly oxidants, a specialty of the CASYEN laboratory. We have previously developed oxidation conditions for the oxidative cleavage of diols under oxygen in the presence of a recyclable heterogeneous catalyst.

The search for oxidation conditions that allow selective access to diols, hydroxyketones or diketones will be part of the work of the PhD student recruited. He/she will also have to apply the newly developed conditions to other terpenes in order to evaluate a wide range of compounds. The physicochemical properties of the compounds will have to be evaluated (DSC, TG, etc.). The evaluation of the repellent properties will be carried out in Madagascar in our associated laboratory.

<u>Candidate profile</u>: The candidate should have a strong background in organic chemistry (M2 degree) and should be motivated to develop catalytic methods in a green chemistry context.