Use of glycerodendrimers for essential oil encapsulation with slow release adapted for biosourced herbicides

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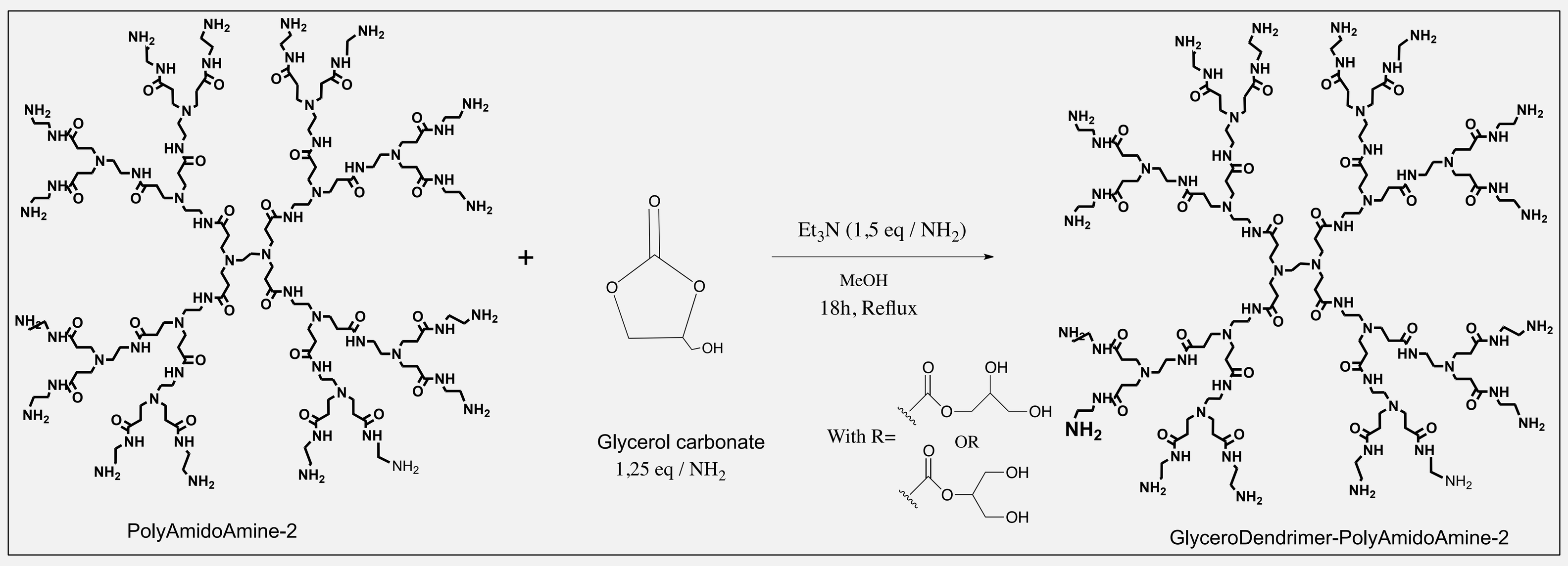
Context

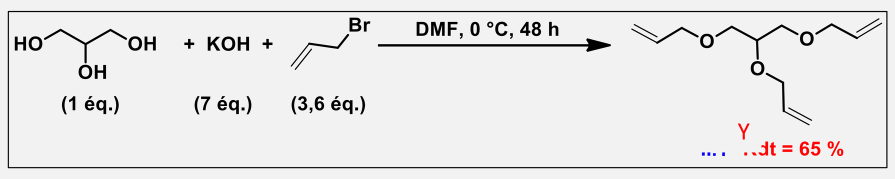
Following the objective of reducing the use of chemical pesticides without decreasing crop yield, essential oils (EOs) are a prime candidate for biocontrol. Encapsulation of them allow to increase the duration of their natural bioactivities. In this work, an innovative green matrix for essential oil retention is proposed: glycerodendrimers (GDs). Some of them have already shown their ability to encapsulate some metallic complexes and organic compounds[3,4] and two very new types has been use.

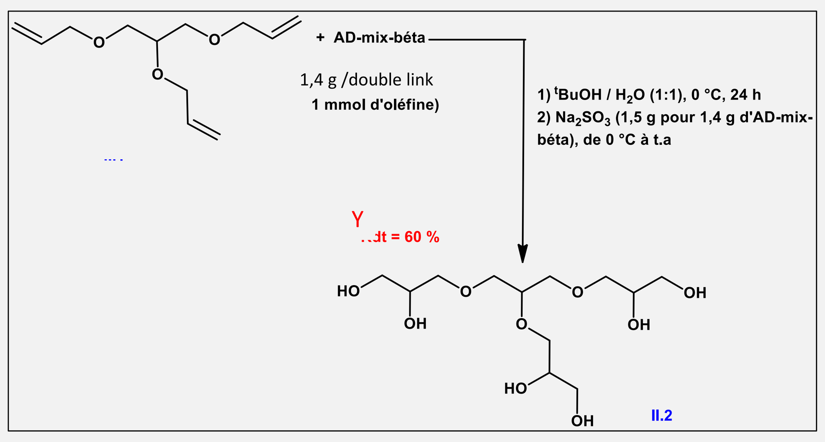
I Synthesis[3,4]

❖ Commercial dendrimer (PAMAM) decoration with glycerol derivatives

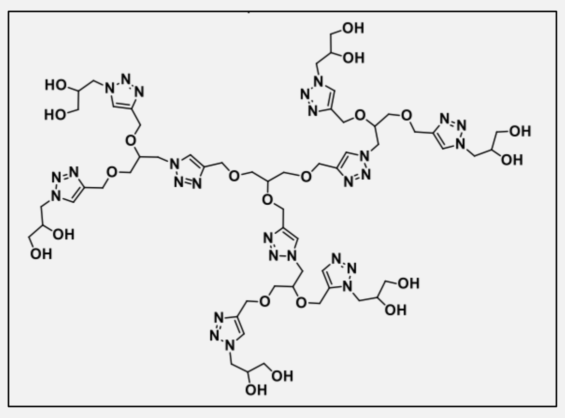


❖ Synthesis of GlycerolAdendrimer by allylation/oxidation of glycerol



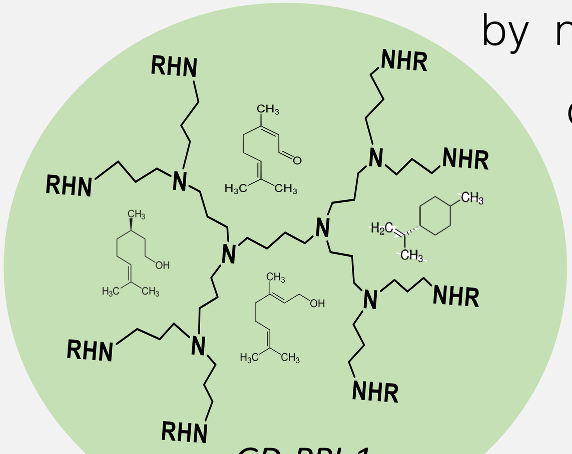


❖ GlyceroClickDendrimer



Objectives

First, synthetize biosourced dendrimers with glycerol derivatives (**I**). Then use it for EOs encapsulations of citronella and cinnamon essential oils, which have been chosen for their herbicide properties. The total retention rate in solution was determined by dynamic headspace gas chromatography coupled with mass spectrometry[2] (**II**). Furthermore, interactions between GDs and EOs were studied by nuclear magnetic resonance spectrometry (**III**). In parallel, efficiency of created products has been controlled by analysing the inhibition of *Arabidopsis thaliana* seed germination (**IV**).



GD-PPI-1 encapsulating citronella EO

II Encapsulation

❖ Dynamic Headspace - Gas Chromatography – Mass Spectrometry

→ EOs retention in aqueous solution

- 4 dendrimers type, each in several generations:
- 2 EOs

Results:
Yield of total retention[2]

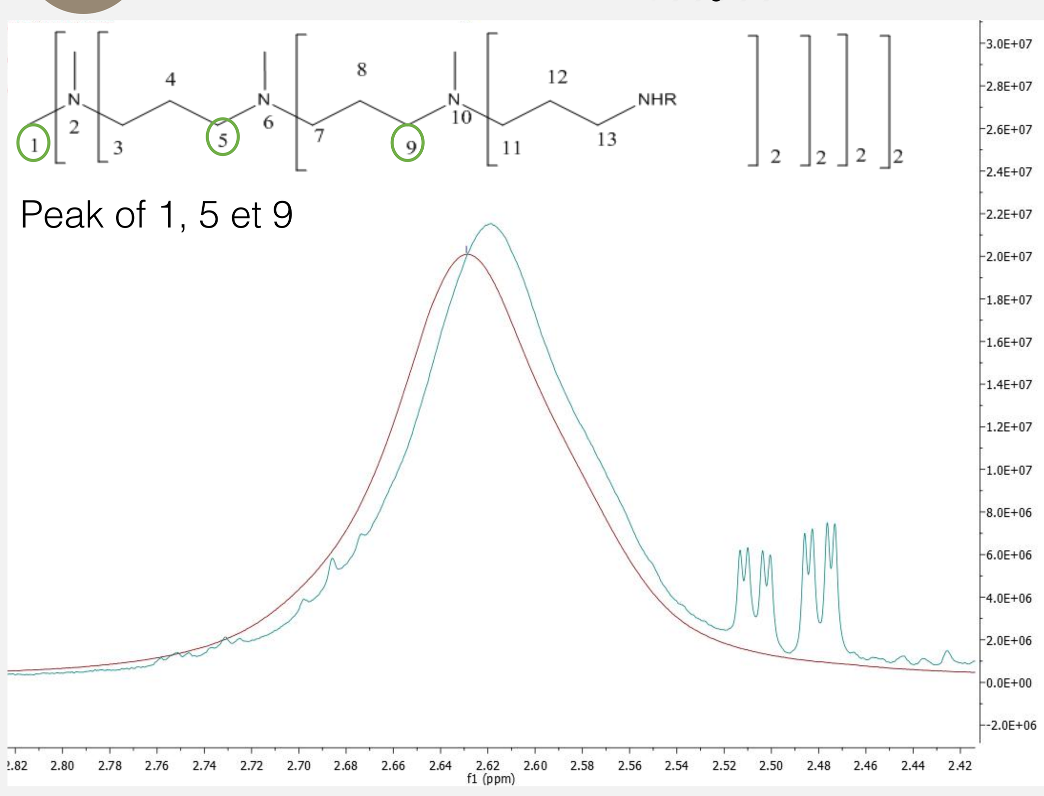
$$r(\%) = \left(1 - \frac{\sum A_D}{\sum A_0}\right) \times 100$$

A_D = Area with dendrimers
A_0 = Area without dendrimers

— (red line) Best retentions
/ No retention

Dendrimer	Citronella EO r(%)	Cinnamon EO r(%)
GD-PAMAM-0	9,83 +/- 0,44	12,17 +/- 0,41
GD-PAMAM-1	6,49 +/- 0,72	29,01 +/- 0,68
GD-PAMAM-2	24,88 +/- 4,80	38,84 +/- 0,57
GD-PAMAM-3	20,39 +/- 2,38	32,97 +/- 1,13
GD-PPI-1	/	24,35 +/- 4,23
GD-PPI-2	3,09 +/- 1,95	14,15 +/- 3,77
GD-PPI-3	26,65 +/- 5,77	25,99 +/- 4,36
GD-PPI-4	10,55 +/- 3,53	24,21 +/- 3,95
GlycéroClickdend-1	/	13,67 +/- 1,57
GlycéroClickdend-2	/	9,37 +/- 2,54
GlycéroClickdend-3	/	/
GlycéroAdend-1	3,89 +/- 1,27	16,23 +/- 5,30
GlycéroAdend-2	/	23,38 +/- 2,85
GlycéroAdend-3	8,28 +/- 1,45	/

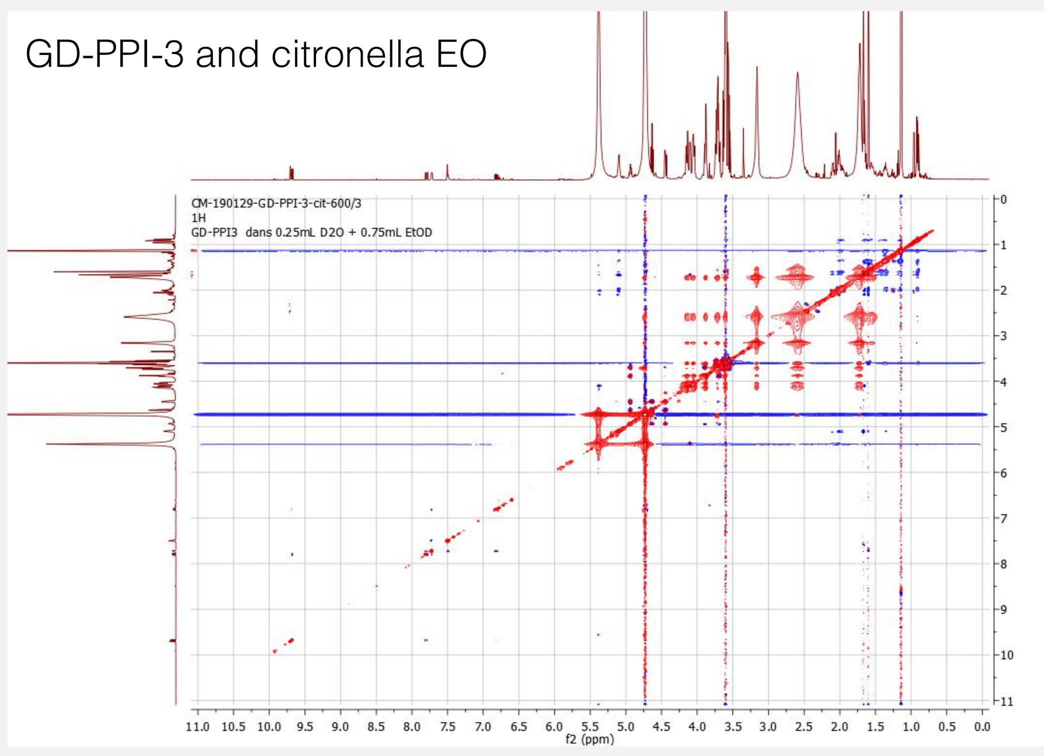
III Interactions



RMN ^{1}H

Principle:
Superposition of ^{1}H RMN spectra
red curve: GD-PPI-3 alone
blue curve: GD-PPI-3 with citronella EO

Result:
Shift of one peak→ electrostatic interactions between dendrimer and EO



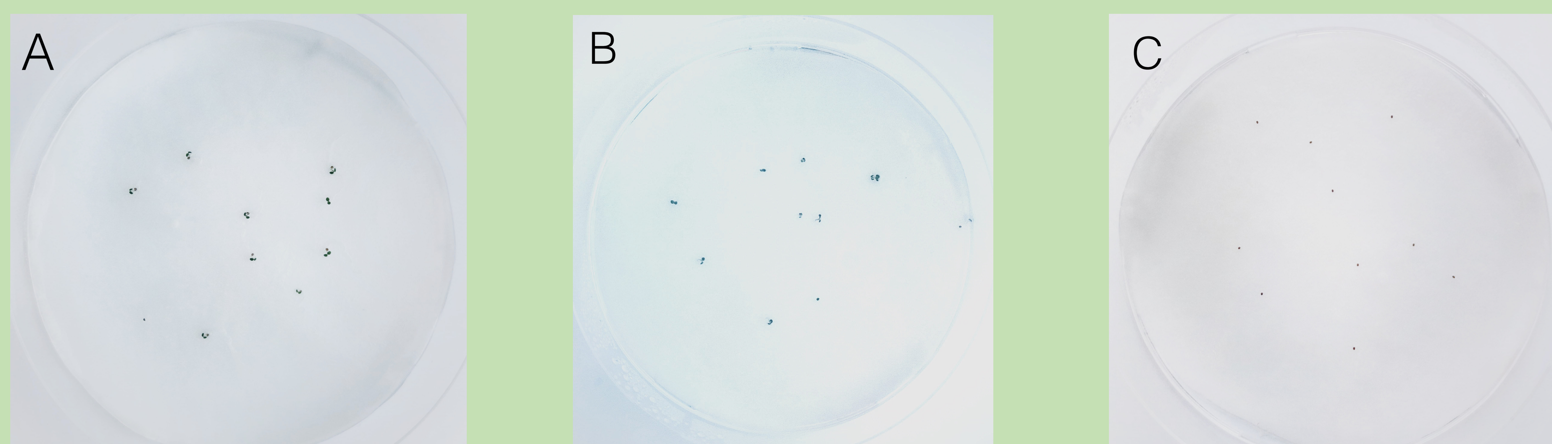
RMN NOESY

Principle:
2D analysis of RMN spectra which show interaction between ^{1}H in space

Result:
No interaction spots at the cross between EO peaks and dendrimer peaks → interactions are more spaced than 5 A°

IV Germination inhibition

Tests of germination inhibition have shown the interest in citronella and cinnamon EOs as germination inhibitors. In addition, dendrimers alone do not interfere on the seeds growing but allow the work of EOs.



Germination — *Germination* — *Inhibition of germination*

A. Sample* treated with water
B. Sample* treated with a 2mM aqueous solution of GD-PPI-3
C. Sample* treated with 20 mg citronella EO encapsulated in a 2mM aqueous solution of GD-PPI-3

* 10 *Arabidopsis thaliana* (L.) Heynh. seeds in petri dish with paper filter; treated with 2mL of solution, closed and incubate 5 days in grow room (16:9 ; 20°C)

Conclusion and perspective

This study shows that essential oil encapsulation by dendrimers is possible and is different following their size. The best generation for each dendrimer type is kept for an optimization of the encapsulation conditions to increase retention yield. RMN analysis show some chemical interactions, more analysis will help to understand nature of these one. Germination inhibition tests performed with the essential oil-dendrimer system confirm the interest of essential oil for biosourced pesticide.

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