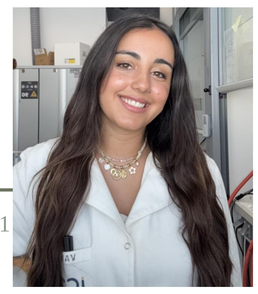
Synthesis of biobased rheology modifiers for cosmetic applications



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Context

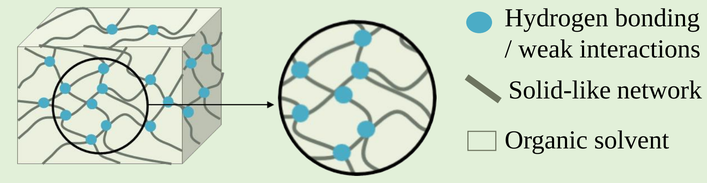
Organo-gelators are mainly used in cosmetic applications due to their ability to enhance the stability, texture, and delivery properties of active ingredients[1].

They are used in a variety of personal care products to create gelled formulations (lipstick, sunscreen, lotions…). They are an alternative to traditional thickeners and emulsifiers[1].

What is an organogelator?

Organo-gelators are compounds capable of immobilizing organic liquids into semi-solid, gel-like structures through self-assembly[2].

The organogel successful formation depends on the **organic phase**, **temperature**, **process time** and characteristics of the **gelling molecules**



State of the art

Biobased traditional thickeners[1] :

- Lecithin
- Glyceryl fatty acid esters
- Sorbitan-derived esters
- Fatty acids and fatty alcohol
- Vegetable waxes

But …

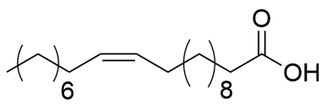
Gelation can result from the synergistic interaction of multiple ingredients, even if none act as gelators individually

→ **opaque** and **non translucent** systems

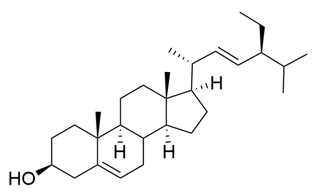
Jojoba oil (*Simmondsia chinensis*)

It does not compete with food resources

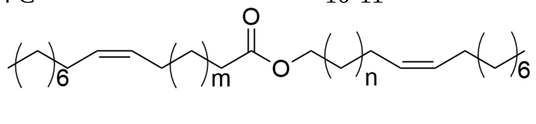
Its annual global production is estimated at 18,000 metric tons[3]



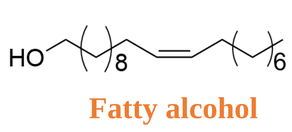
Fatty acid



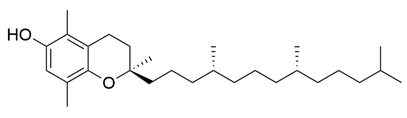
Tocopherols



Wax esters



Fatty alcohol



Sterols (stigmasterol)

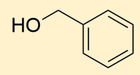
Objectif and strategy of the project

Synthesis of an **organo-gelator**

- Transparency
- Gelation of the oil phase
- 100% biobased
- Jojoba derivative

Functionalization using weakly interacting molecules

Test model with



(π-π stacking)

Polymerization of phenols

Ex. Stilbenes, flavonoids eugenol…

Structure and composition[3]

Alkyl chain length of the wax esters	Weight composition (%wt)
36 C	1-2
38 C	6-7
40 C	26-30
42 C	49-52
44 C	10-11

Use of virgin or refined oil?

Product	Gardner color	Lab	Rancimat : Oxidative Stability Index (OSI) (µs/cm=f(temps))
Virgin Jojoba oil	9	L= 90,22 a= -1.56 b= 89.15	20h
Discoloration of jojoba oil*	0.6	L= 99.46 a= -0.77 b= 3.86	3.3h

**1 wt% activated charcoal, 1 wt% Arbacel; 300 mbar, 80 °C, 1 h → filtration*

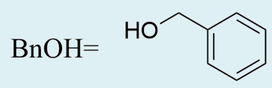
After decolorization, the elimination of natural antioxidants compromises the oil's oxidative stability

→ **ANTIOXIDATING BENEFITS**

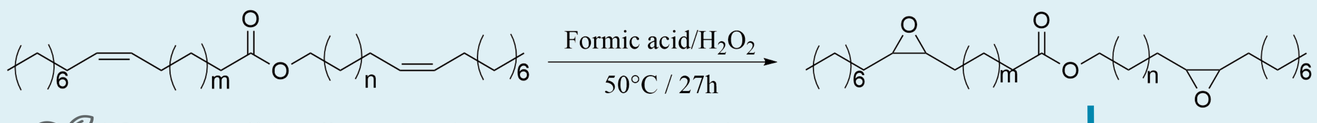
(UHPLC C18 AN/H_2O to see mg/100g of stigmaterol and β-sitosterol)

Chemical functionalization of jojoba oil double bonds

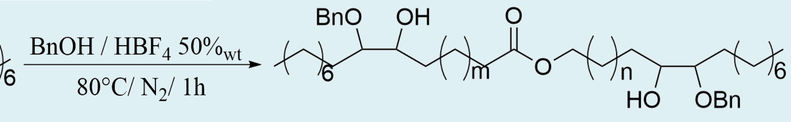
BnOH=



1st step: epoxidation



2nd step: epoxide ring-opening

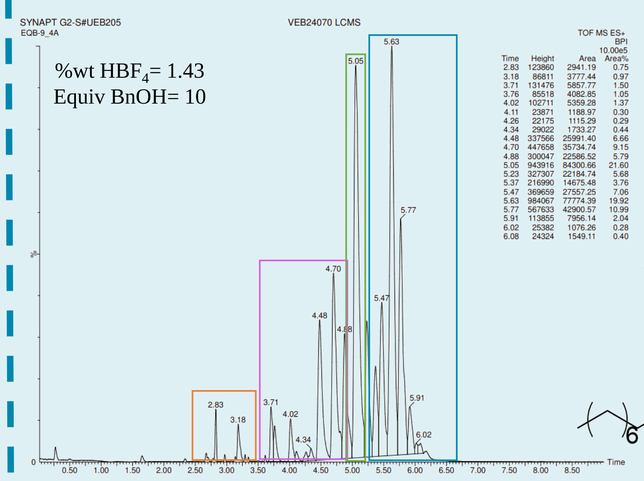


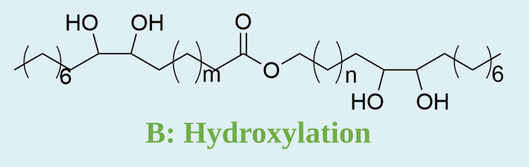
A: Benzylation

- "Green conditions" reaction (≠ mCPBA or Oxone®)
- The reactivity of oxiranes allows for multiple ring-opening pathways
- Not colored product

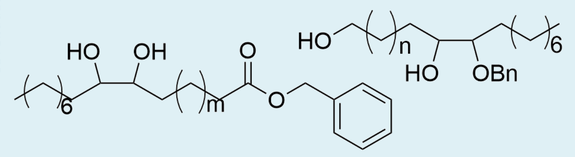
Side reactions (B,C,D) due to oxirane ring-opening with HO-R

IDENTIFICATION OF SIDE PRODUCTS**: liquid chromatography-mass spectroscopy (LC-TOF MS ES+)**

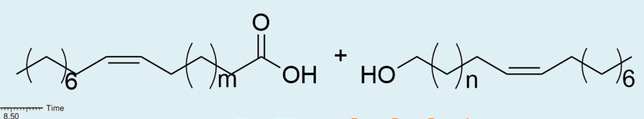




B: Hydroxylation



C: Transesterification



D: Ester hydrolysis

Column**:** Biphenyl 50 × 2.1 mm /**A:** H_2O + 0.1% FA, **B:** ACN + 0.1% FA, **flow rate:** 0.5 mL/min /Gradient**:** from 0 to 100% B in 5 min, then 2 min at 100% B

Time (min)	Molecule mass (m/z)	Identified molecule
5.47	719.6	1 BnO- 3OH 38 C
5.63	747.6	1 BnO- 3OH 40 C
5.77	775.7	1 BnO- 3OH 42 C
5.94	837.7	2 BnO- 2OH 40 C

Various benzylation products are observed for each wax esters type in jojoba oil

Benzylation was promoted by using a small amount of catalyst and a low molar ratio of BnOH

Reaction monitoring by ^{1}H NMR ($CDCl_3$, 400 MHz) spectroscopy[4]

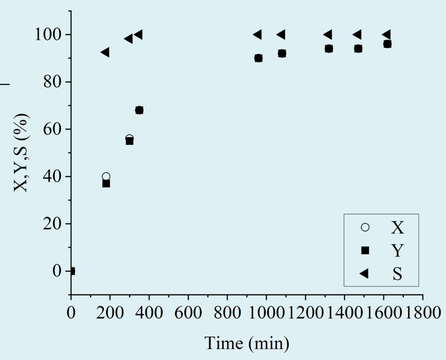
X=conversion (%) **Y= yield (%)** **S= selectivity (%)**

$$DB_{(t)}=\frac{N_{H2.32}A_{5.36(t)}}{N_{H5.36}A_{2.32}} \quad Epox_{(t)}=\frac{N_{H2.32}A_{2.90(t)}}{N_{H2.90}A_{2.32}} \quad S=\frac{Y}{X}$$

$$X=\frac{DB_0-DB_{(t)}}{DB_0} \quad Y=\frac{Epox_{(t)}}{DB_0}$$

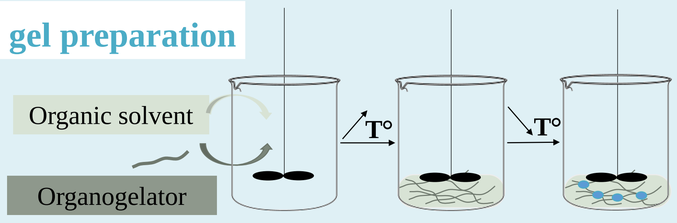
Best result at t_f: X=97%, Y=97%, S=100%

- **DB_0:** amount of double bonds of the starting material, **$DB_{(t)}$:** amount of double bond during the reaction time
- Signals at **5.36 ppm**: olefinic protons [-CH=CH-] (∫4H), **2.90 ppm**: epoxy group [-CHOCH-] (∫4H), **2.32 ppm**: α-carbonyl protons [-$COCH_2CH_2$] (∫2H)

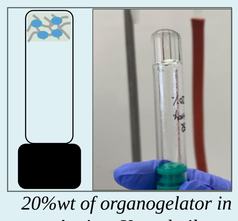


Kinetics of double bond conversion to epoxide over time by ^{1}H NMR

3rd step: gel preparation



« Inversion tube test »



20%wt of organogelator in Apricot Kernel oil

Conclusion

The model study clarified the chemical behavior of Jojoba oil, in particular its epoxidation and subsequent benzylation via epoxide ring-opening.

This strategy allows the introduction of polar functions (hydroxyl, ester, etc.) that can enhance intermolecular interactions and, consequently, the viscosity of the final product (**gel formation**).

References

[1] Martinez, R. M et al. "Main Features and Applications of Organogels in Cosmetics." *International journal of cosmetic science* 41.2 (2019)

[2] Zeng, Liangpeng et al. "Recent Advances of Organogels: From Fabrications and Functions to Applications." *Progress in organic coatings* 159 (2021)

[3] Gad, Heba A et al. "Jojoba Oil: An Updated Comprehensive Review on Chemistry, Pharmaceutical Uses, and Toxicity." Polymers 13.11 (2021)

[4] Cogliano, Tommaso et al. "1H NMR-Based Analytical Method: A Valid and Rapid Tool for the Epoxidation Processes." Industrial crops and products 186 (2022)

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