

Combiner chimie verte, biotechnologies et génie des procédés pour valoriser la biomasse et les co-produits

Louis Mouterde

URD ABI – AgroParisTech





AgroParisTech

- Etablissement d'Enseignement Supérieur et Recherche
- Sous tutelle des Ministères de l'agriculture et de l'ESRI
- Missions :
 - Nourrir les hommes en gérant durablement les territoires
 - Préserver les ressources naturelles
 - Favoriser les innovations
 - Intégrer la bioéconomie
- Forme des cadres, ingénieurs, docteurs et managers dans domaine du vivant et de l'environnement
- Membre fondateur de l'Université Paris-Saclay

Institut des Sciences et Industries du Vivant et de l'Environnement



L'URD Agro-Biotechnologies Industrielles (ABI)



Cathédrale



Champagne



Vigne

- Unité R&D d'AgroParisTech
- Fondée en 2012
- Dirigé par le Pr. Florent Allais
- Financé par les autorités locales

Aux portes de la bioraffinerie de Bazancourt-Pomacle

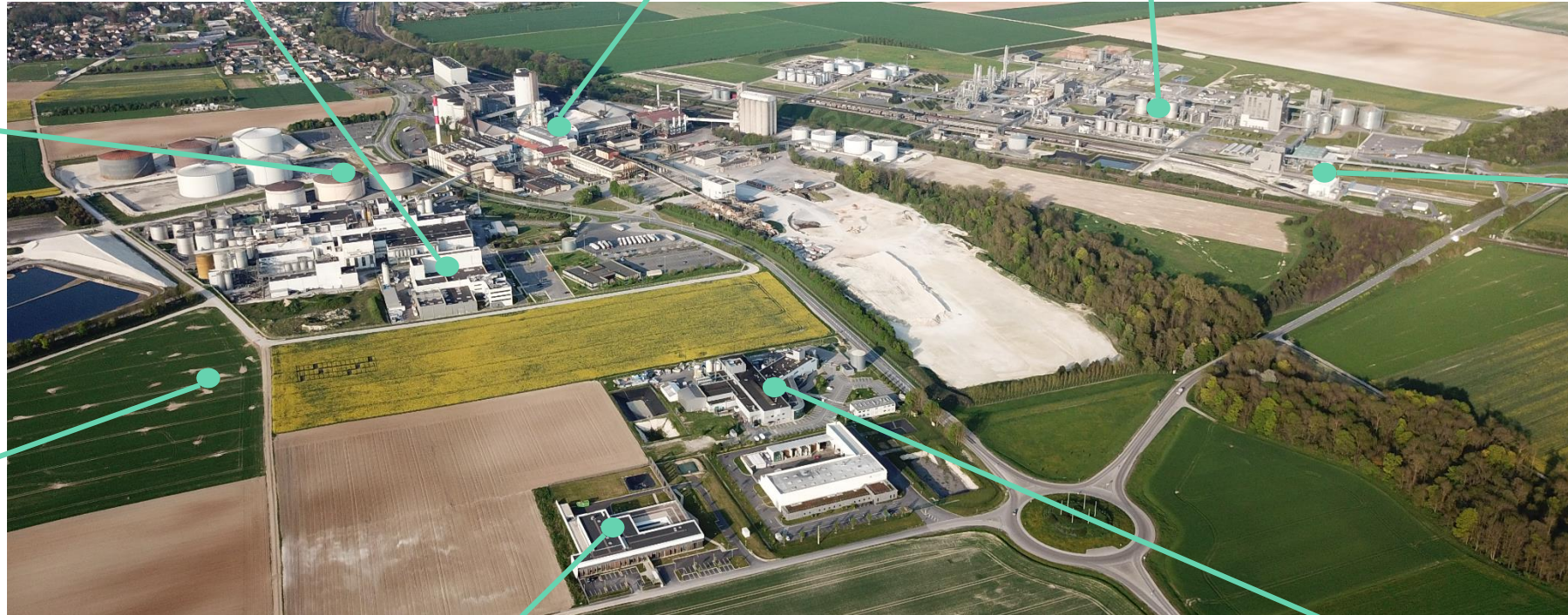
ARD : Centre de recherche privé
Wheatoléo : Tensio-actifs biosourcés

Cristal-Union : Sucrerie
CRISTAL UNION
C'est ensemble que nous avançons.

Cristanol : Distillerie de 1^{ère} génération
CRISTAL UNION
C'est ensemble que nous avançons.

Vivescia : Coopératives céréalières

ADM : Glucoserie et amidonnerie



Air Liquide : Producteur de gazs

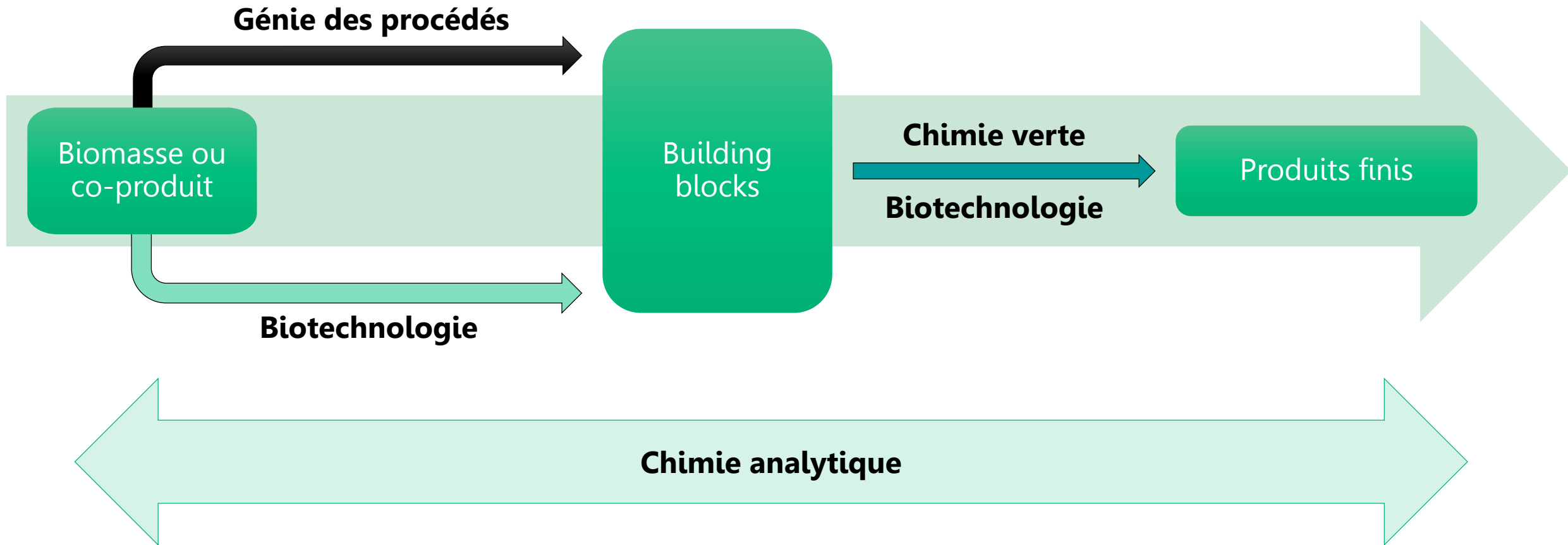
Européenne de Biomasse : Producteur de granulés industriels

CEBB : Centre de recherche public

Givaudan Active Beauty : Cosmétiques biosourcés

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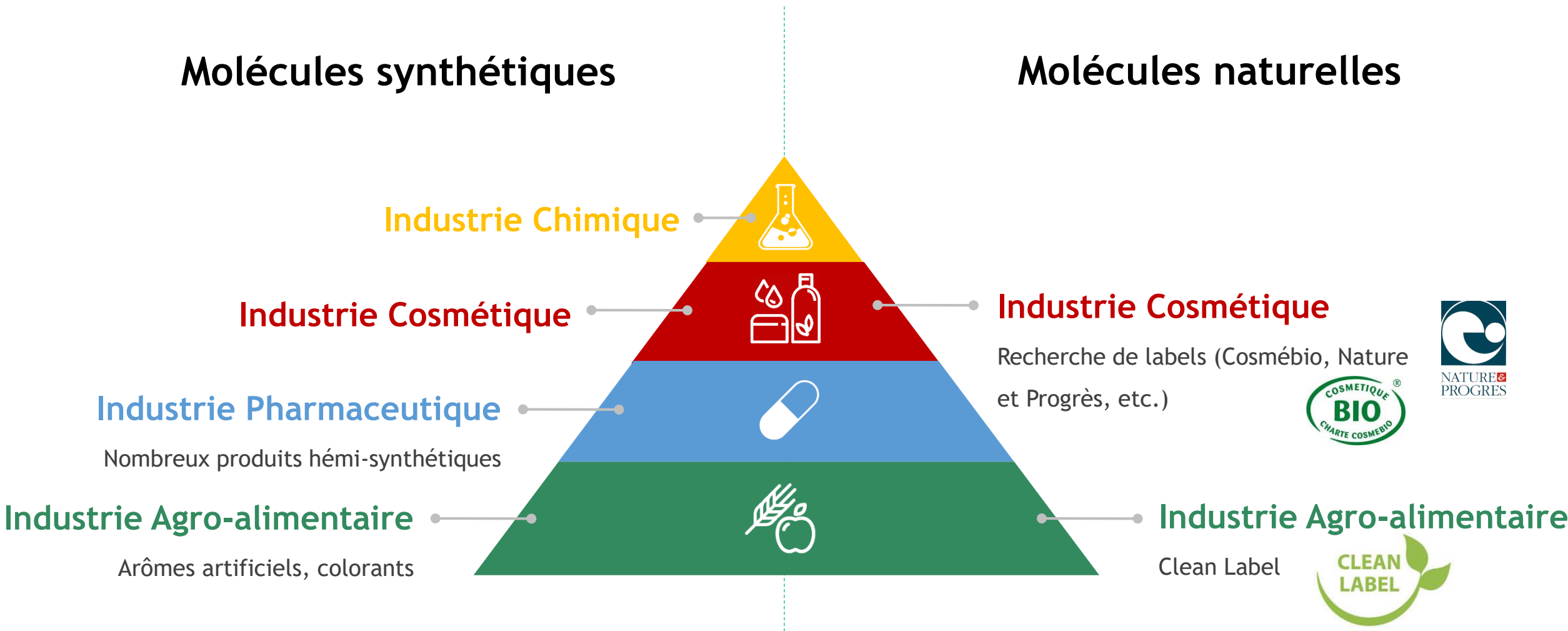
Approche stratégique globale



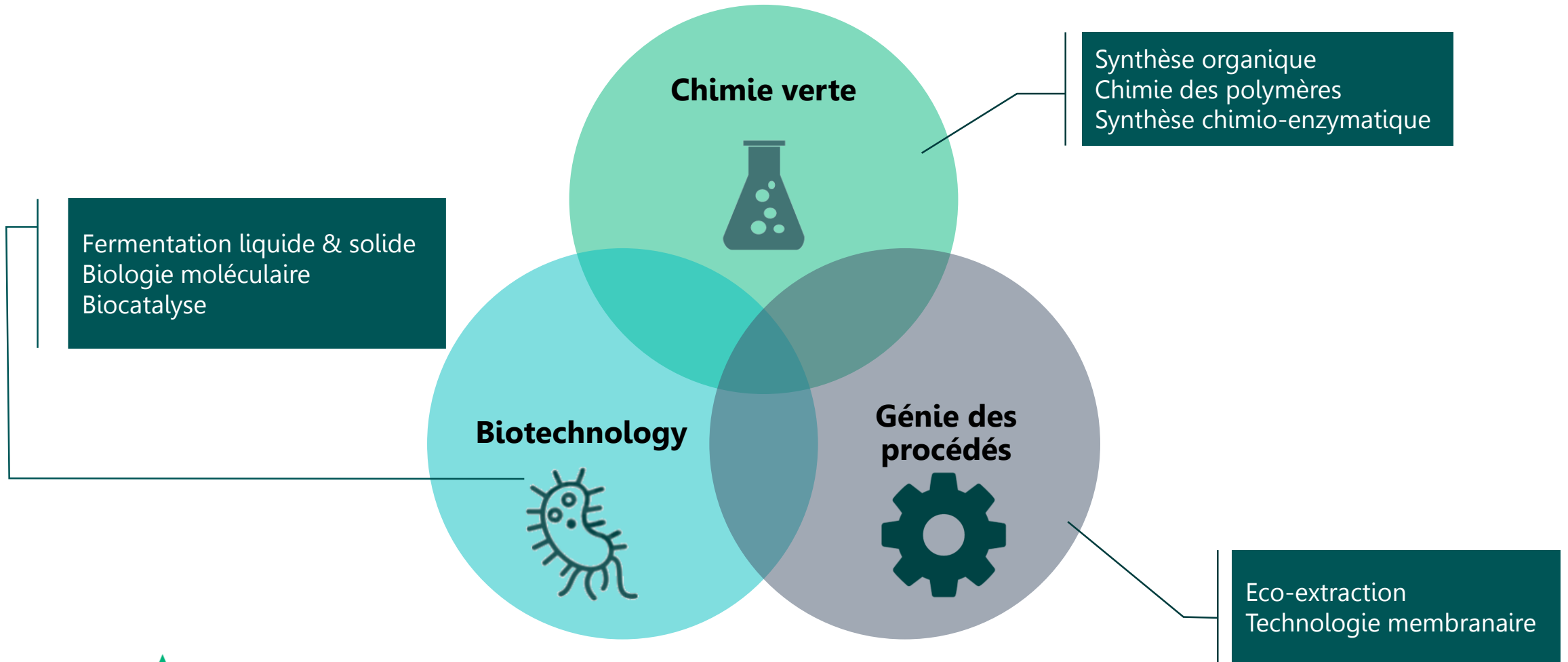
Synthétique vs naturel

Molécules synthétiques

Molécules naturelles



URD ABI : Une unité R&D transdisciplinaire



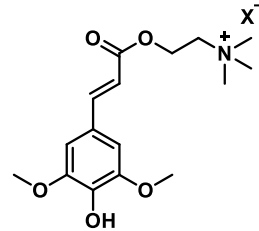


Les acides *p*-hydroxycinnamiques



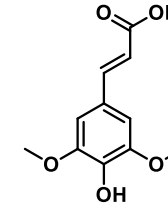
Son de Moutarde

Extraction
Liquide/solide

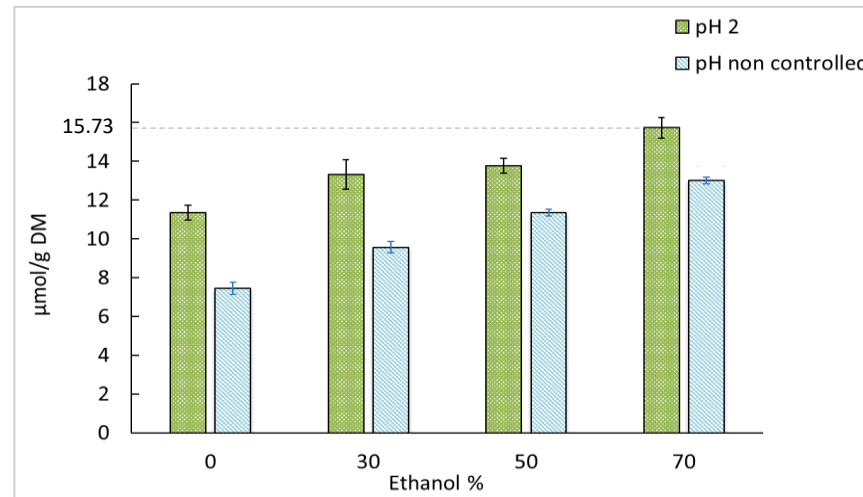


Sinapine

Hydrolyse



Acide sinapique



Evolution de la teneur en sinapine extraite du son de moutarde à pH2 et à pH non contrôlé.

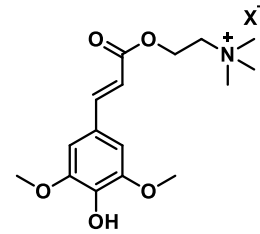


Les acides *p*-hydroxycinnamiques



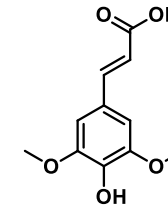
Son de Moutarde

Extraction
Liquide/solide

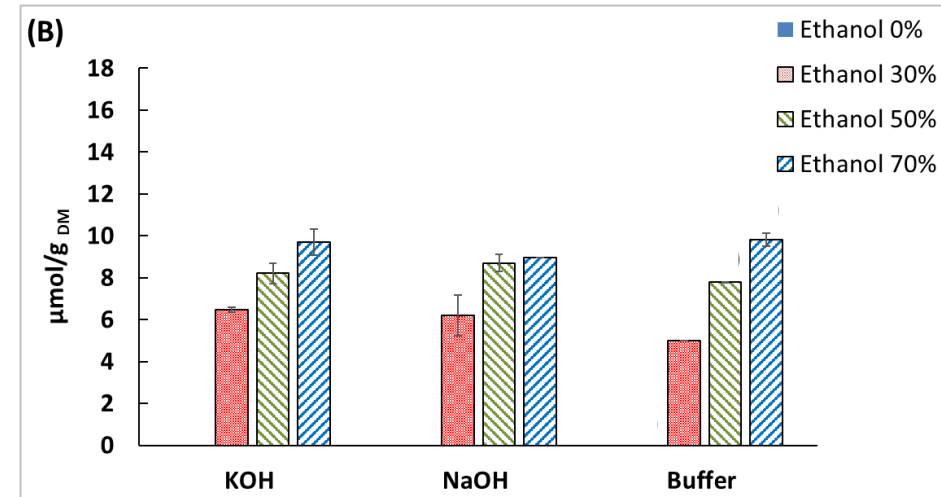
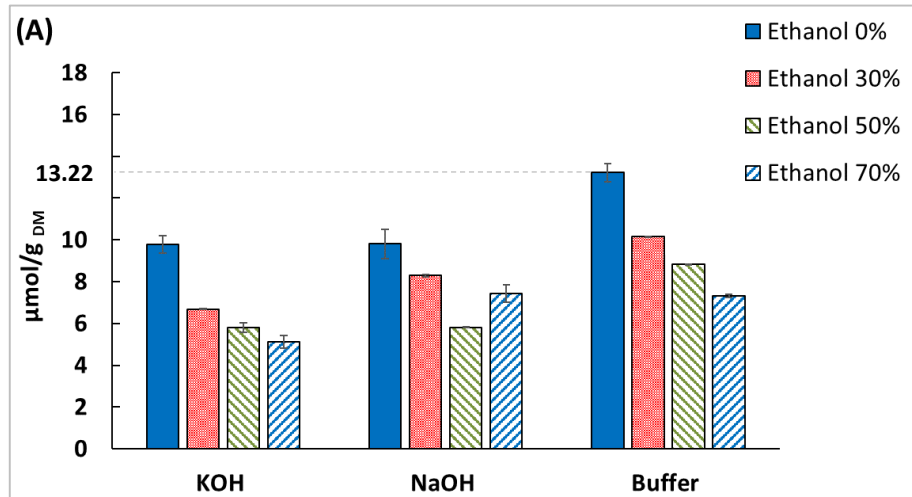


Sinapine

Hydrolyse



Acide sinapique



Teneurs en acide sinapique (A) et en sinapate d'éthyle (B) obtenues à pH 12 à différent pourcentage d'éthanol



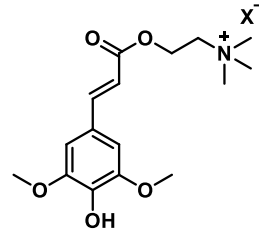


Les acides *p*-hydroxycinnamiques



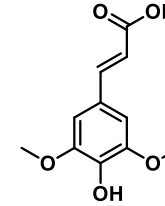
Son de Moutarde

Extraction
Liquide/solide

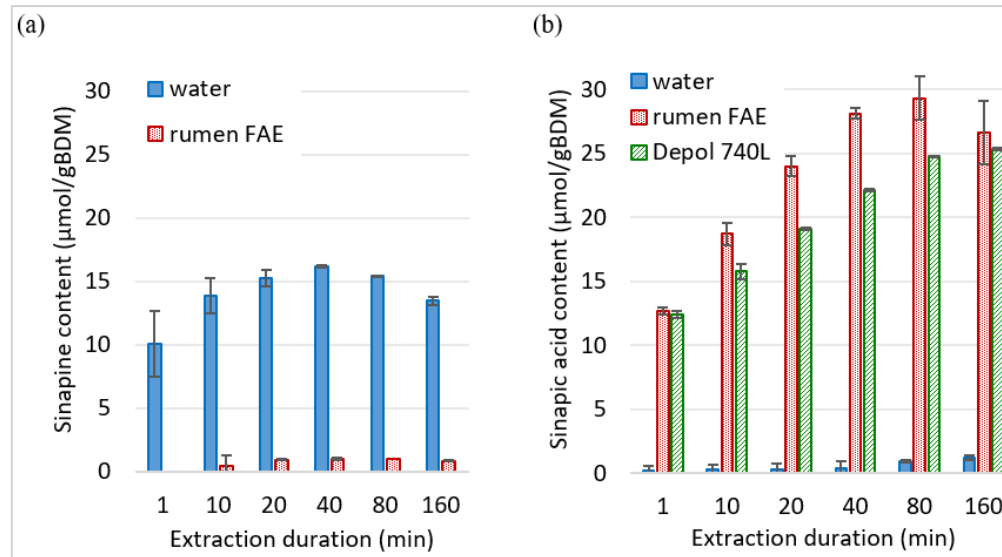


Sinapine

Hydrolyse
enzymatique



Acide sinapique



Teneur en Sinapine (a) et en acide sinapique (b) extrait du son de moutarde en présence de Depol 740L, rumen FAE et eau à 50 °C, pH 7.





Les acides *p*-hydroxycinnamiques

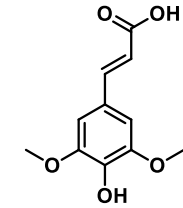


Son de Moutarde

Extraction
Liquide/solide



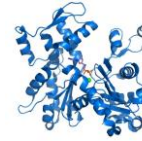
Hydrolyse
enzymatique



Acide sinapique

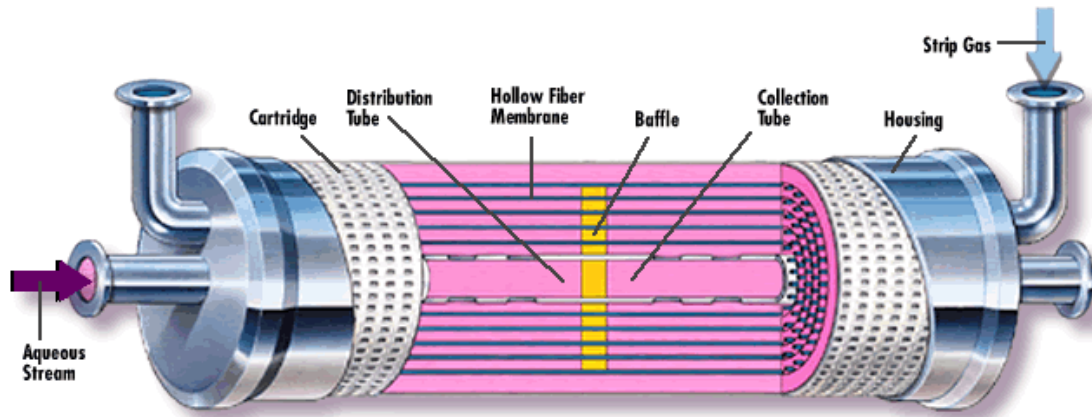


Sucres

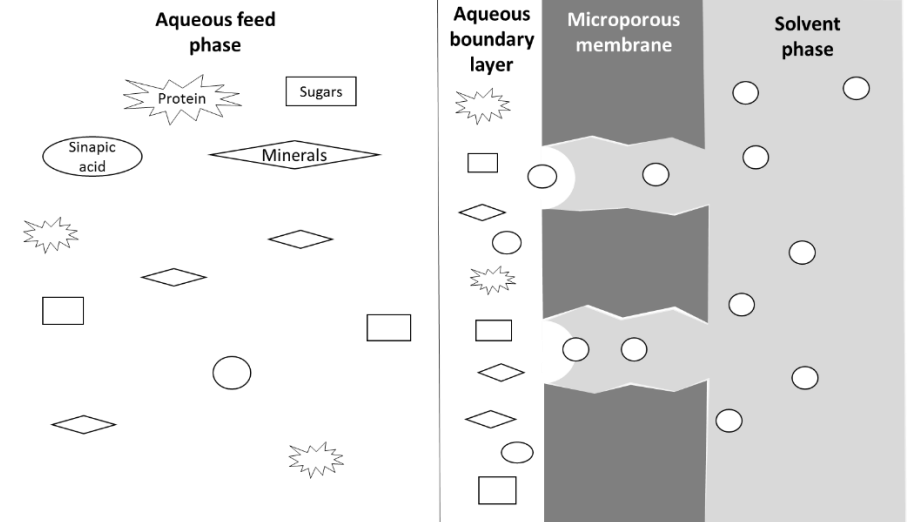


Protéines

Contacteur membranaire



2 phases non miscibles sont mises en contacts *via* des fibres creuses poreuses

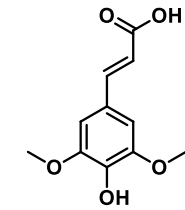




Les acides *p*-hydroxycinnamiques



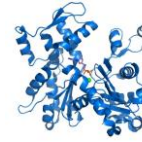
Son de Moutarde

Extraction
Liquide/solideHydrolyse
enzymatique

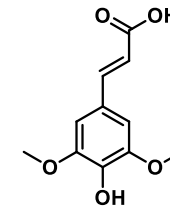
Acide sinapique



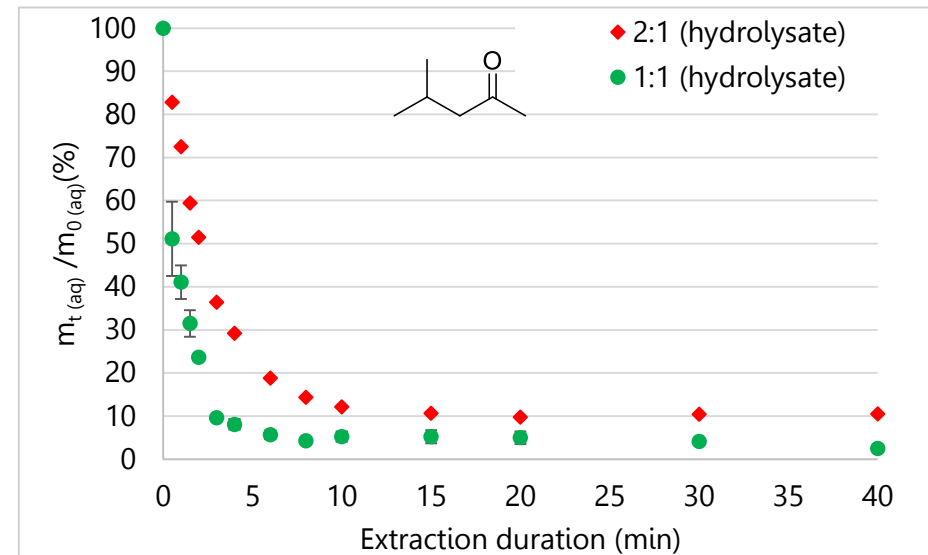
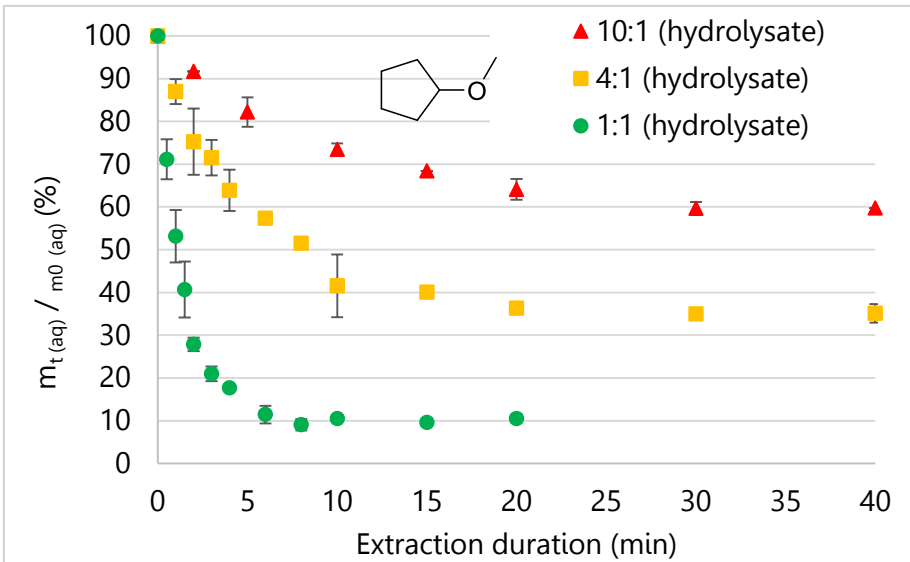
Sucres



Protéines

Contacteur
membranaire

Acide sinapique



Cinétique d'extraction de l'acide sinapique, issu de son de moutarde, dans le CPME ou le MIBK



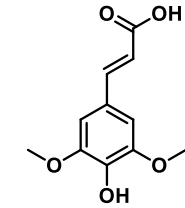


Les acides *p*-hydroxycinnamiques



Son de Moutarde

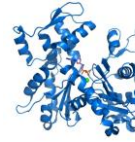
Extraction
Liquide/solide
Hydrolyse
enzymatique



Acide sinapique

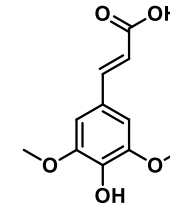


Sucres



Protéines

Contacteur
membranaire

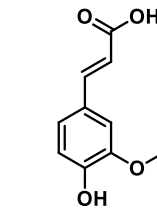


Acide sinapique



Son dé blé

Extraction
Liquide/solide
Hydrolyse
enzymatique



Acide férulique

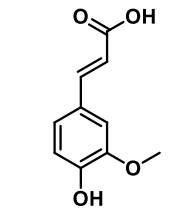


Sucres



Protéines

Contacteur
membranaire

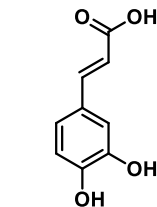


Acide férulique



Racines d'endives

Extraction
Liquide/solide
Hydrolyse
enzymatique



Acide caféique

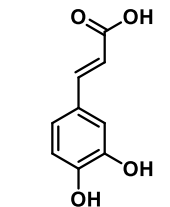


Sucres



Protéines

Contacteur
membranaire

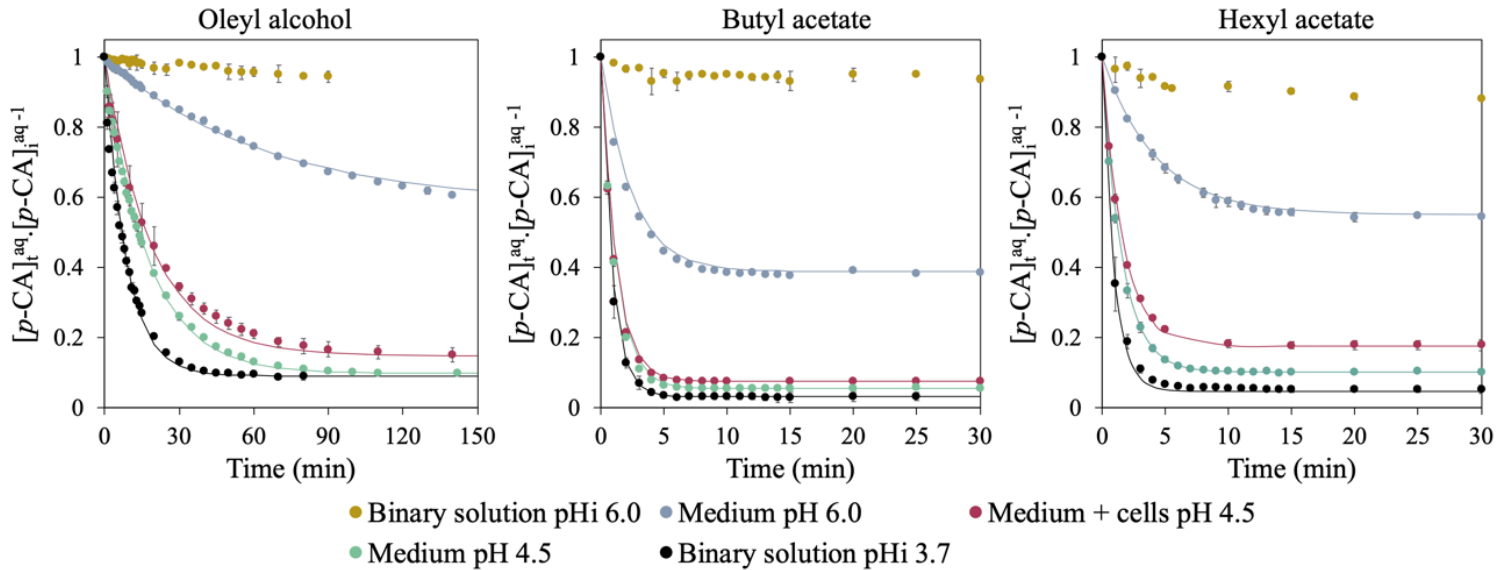
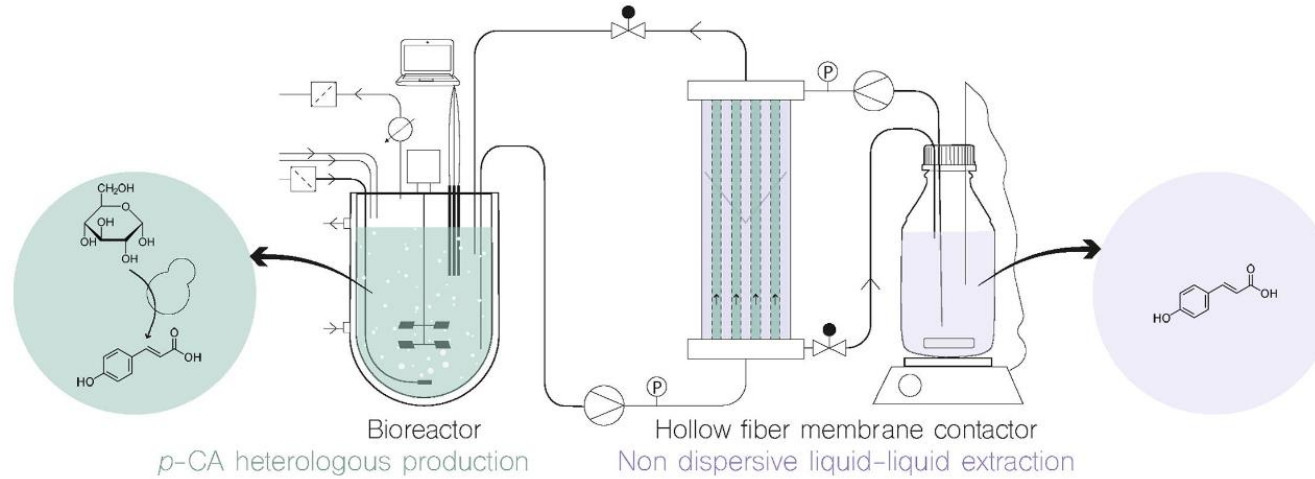


Acide caféique





Les acides *p*-hydroxycinnamiques



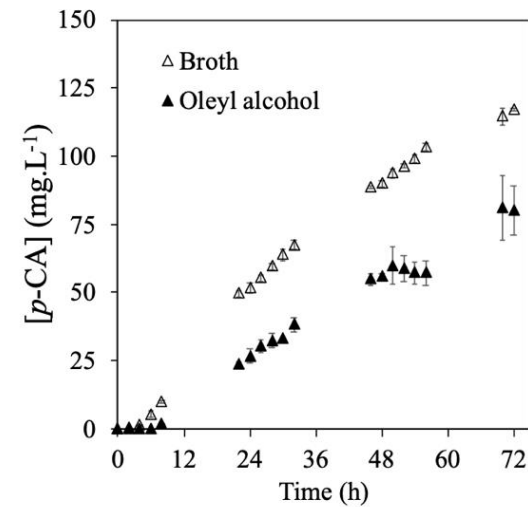
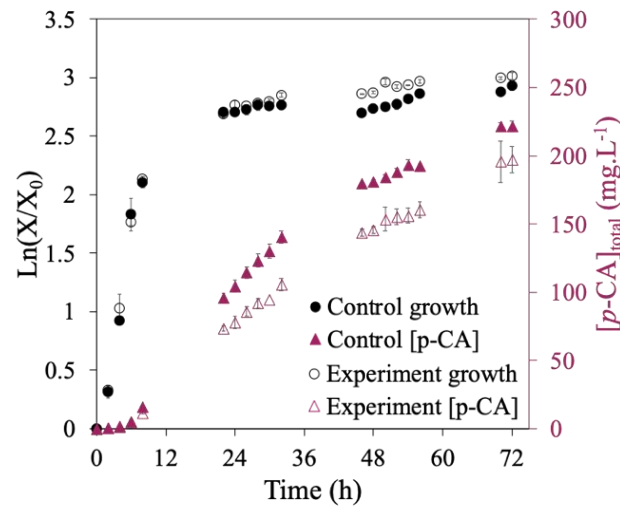
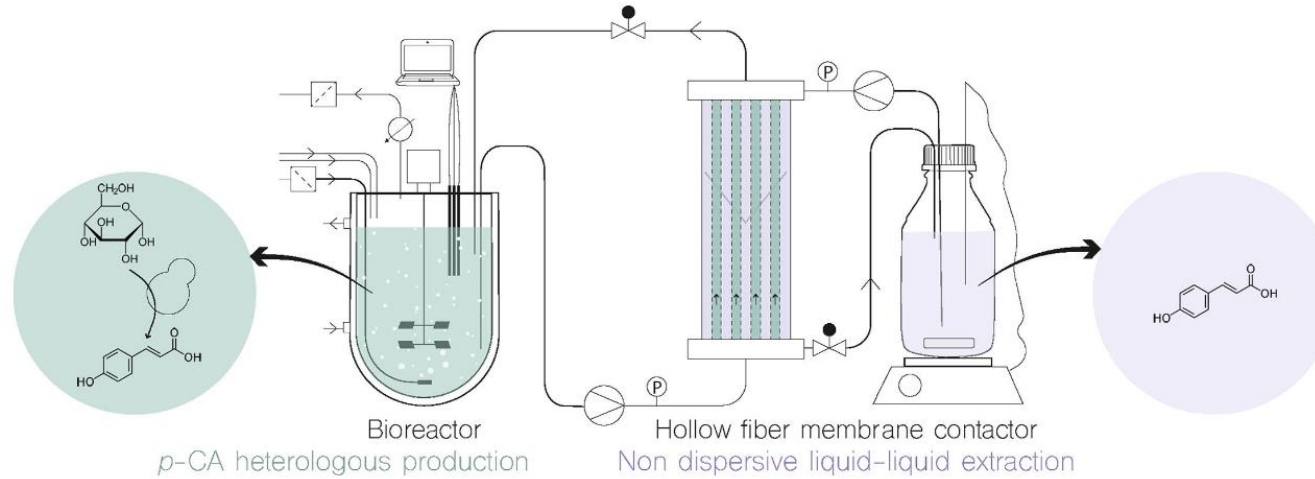
Génie des procédés



Biotechnologie



Les acides *p*-hydroxycinnamiques



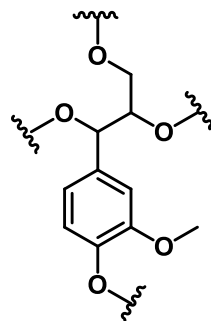


Les acides *p*-hydroxycinnamiques

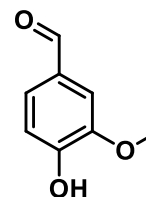


Lignine

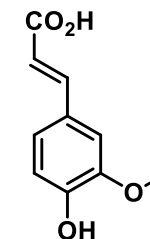
G-units



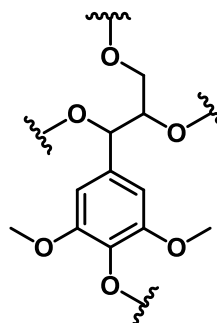
Oxidation


 Proline, EtOH
 Acide malonique
 90 °C, 16h

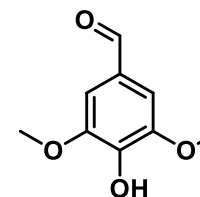
69%



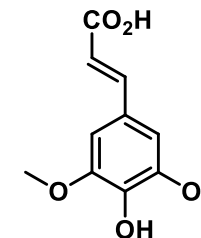
S-units



Oxidation


 Proline, EtOH
 Acide malonique
 90 °C, 16h

85%



Biotechnologie



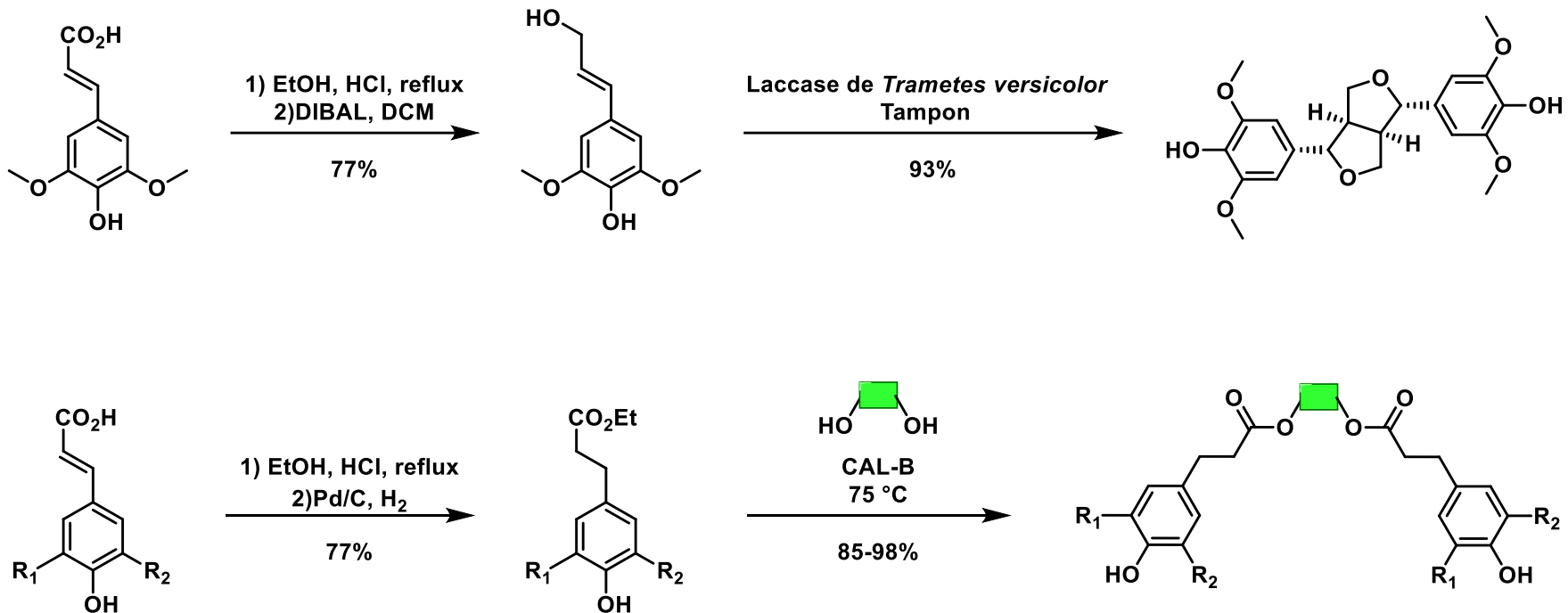
Chimie verte



Les acides *p*-hydroxycinnamiques



Substituts au BPA



URD ABI

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Pion, F. *et al.* RSC Adv. **2013**, 3, 8988

Teixeira A. *et al.* React. Chem. Eng. **2017**, 2, 406

Jaufurally A.S. *et al.* ChemistrySelect **2016**, 1, 5165



Biotechnologie



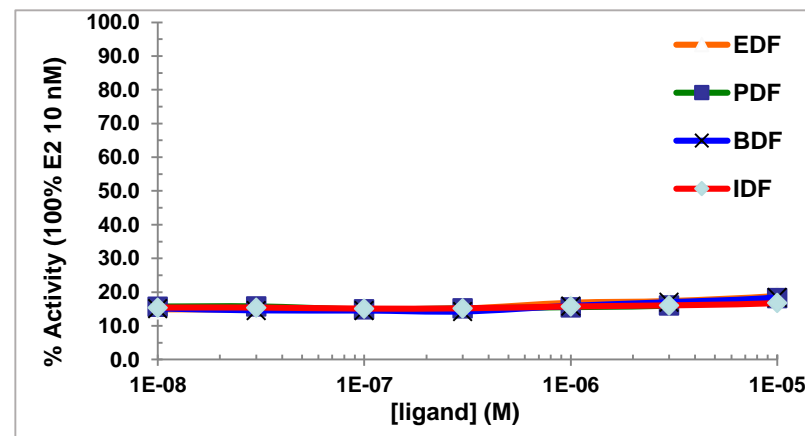
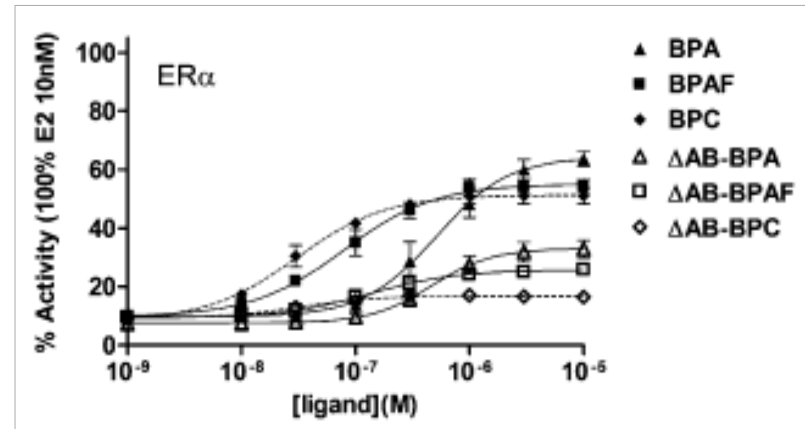
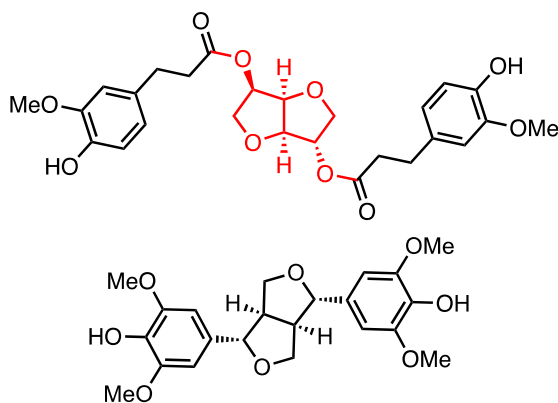
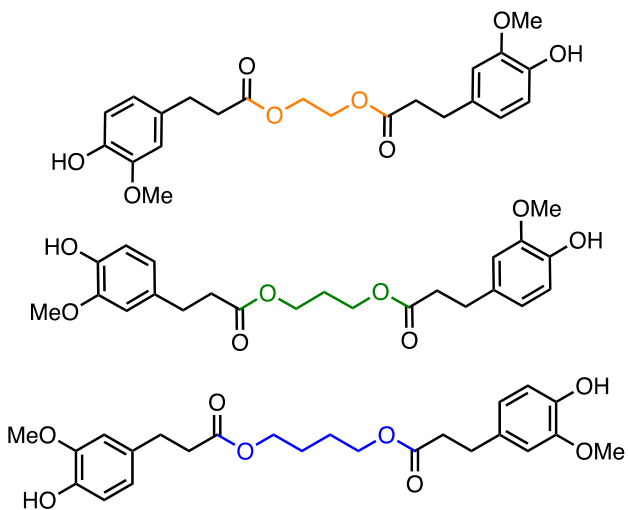
Chimie verte



Les acides *p*-hydroxycinnamiques



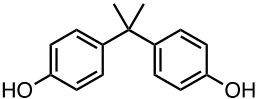
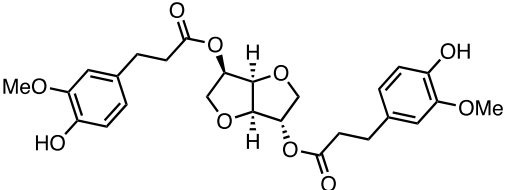
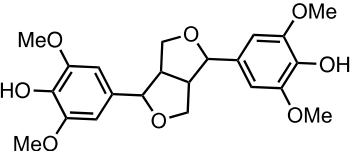
Substituts au BPA





Substituts au
BPA

Les acides *p*-hydroxycinnamiques

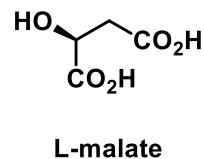
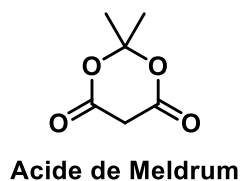
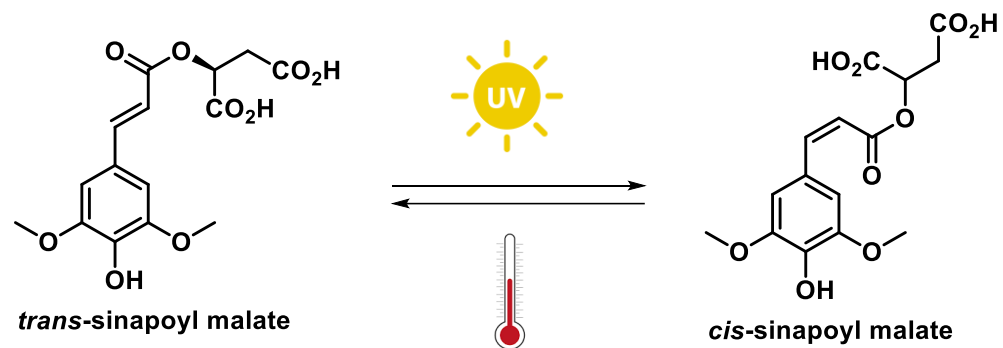
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Sourcing	<input checked="" type="checkbox"/> Pétrole	<input checked="" type="checkbox"/> Acide férulique	<input checked="" type="checkbox"/> Acide sinapique	
Toxicité	<input checked="" type="checkbox"/> Perturbateurs endocriniens	<input checked="" type="checkbox"/> Non Perturbateurs endocriniens	<input checked="" type="checkbox"/> Non Perturbateurs endocriniens	
EPOXY-AMINE RESINS	Propriétés mécaniques	<input checked="" type="checkbox"/> $T_g = 150 \text{ °C}$ <input checked="" type="checkbox"/> $T_\alpha = 166 \text{ °C}$ <input checked="" type="checkbox"/> $T_{deg} = 326 \text{ °C}$	$T_g = 85 \text{ °C}$ $T_\alpha = 99 \text{ °C}$ $T_{deg} = 295 \text{ °C}$	<input checked="" type="checkbox"/> $T_g = 126 \text{ °C}$ <input checked="" type="checkbox"/> $T_\alpha = 157 \text{ °C}$ <input checked="" type="checkbox"/> $T_{deg} = 298 \text{ °C}$
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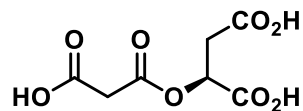


Les acides *p*-hydroxycinnamiques

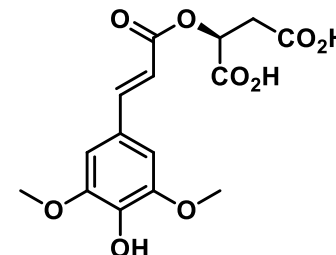
Le Sinapoyl malate: le filtre UV des plantes



Sans solvant
95 °C, 2h

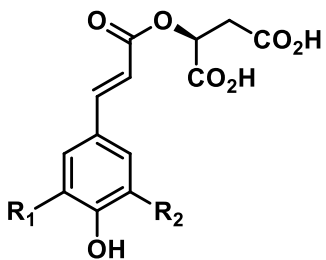


Proline, EtOH
90 °C, 16h
50%



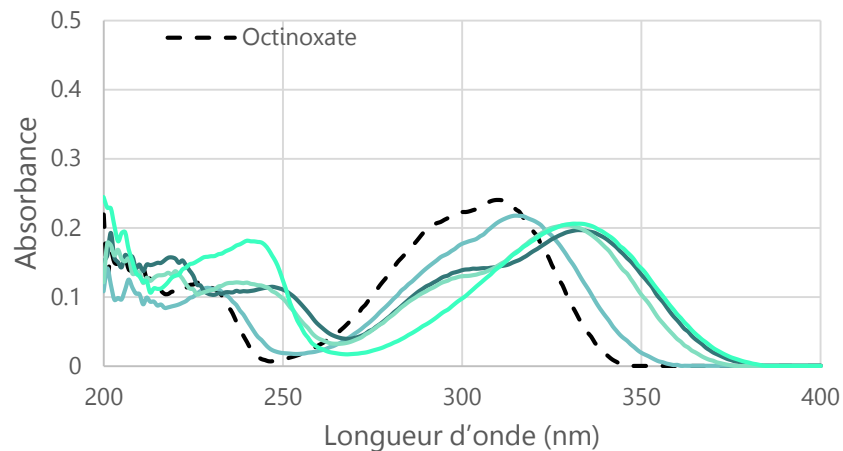


Anti-UV

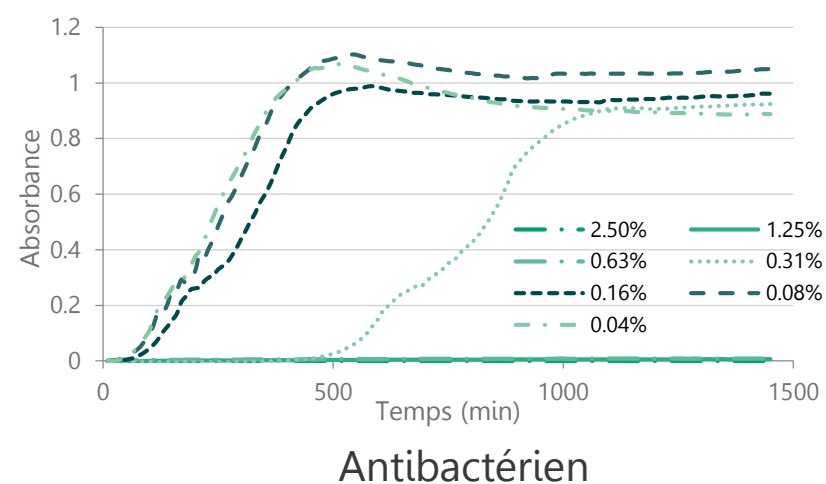
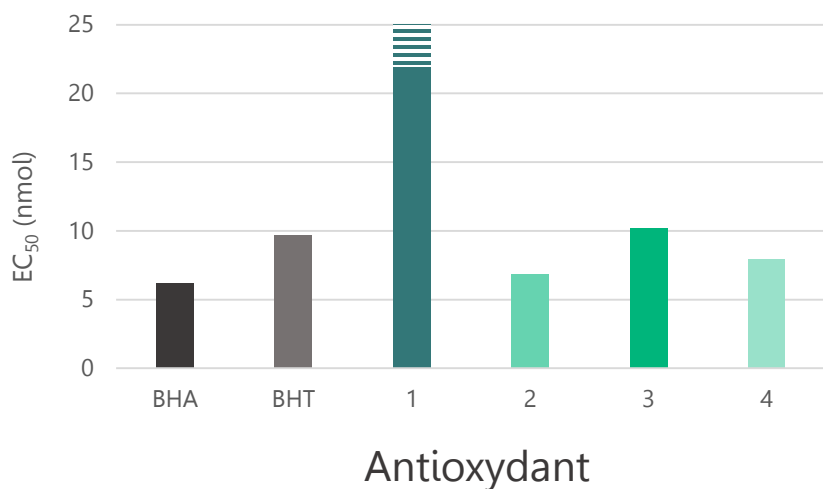
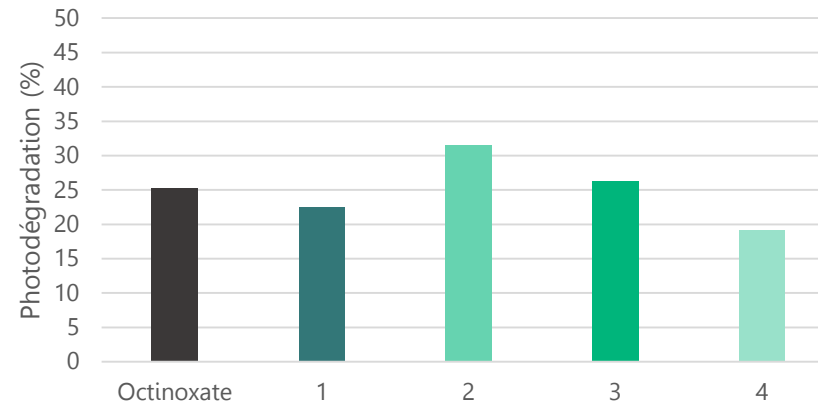


Les acides *p*-hydroxycinnamiques

Couverture UV



Stabilité UV



Chimie verte

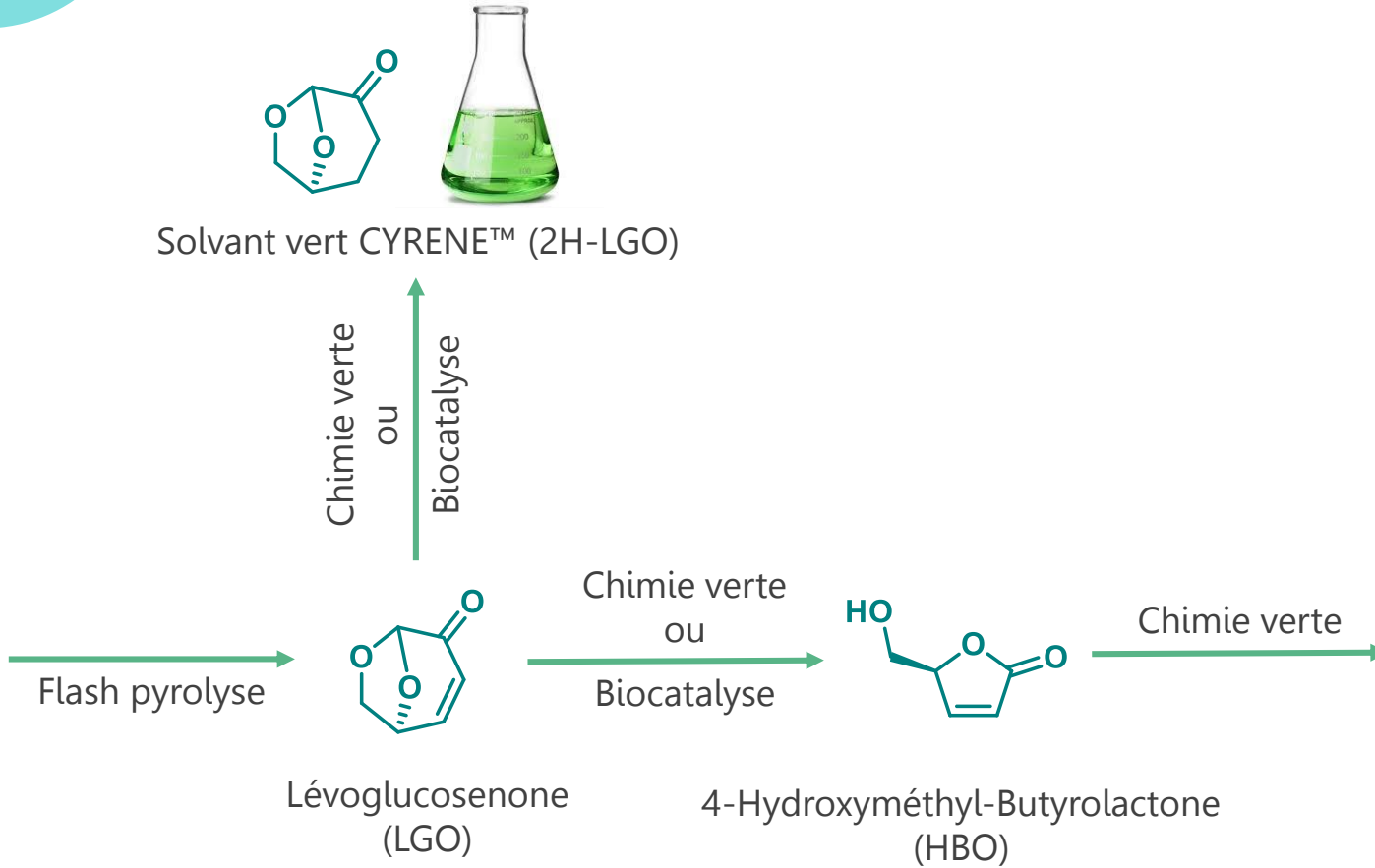
Biotechnologie



La Lévo-glucosénone



Cellulose



Intermédiaires pharmaceutiques

Phéromones

Sucres rares

Tensioactifs

Arôme beurre



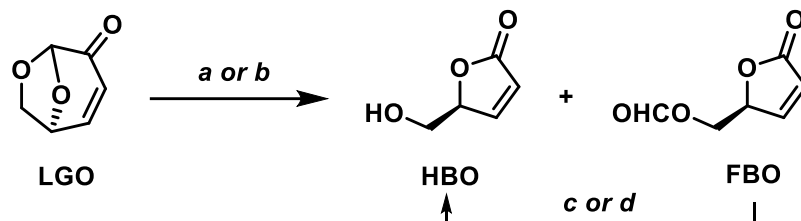
Chimie verte



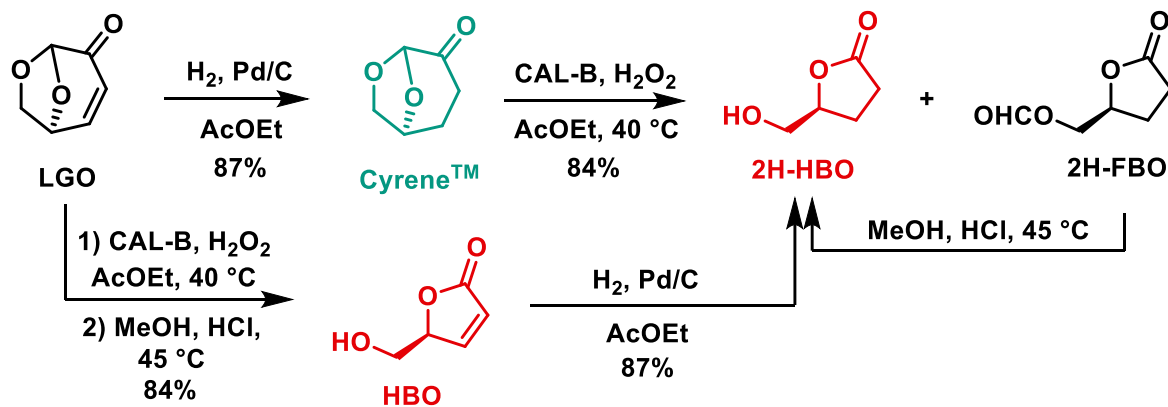
Biotechnologie



La Lévo-glucosénone



Koseki's procedure: a) MCPBA or AcOOH, Me₂S, 48h, rt
c) MeOH, HCl, 45 °C, overnight
Paris' procedure: b) Metal-Zeolite, 100 °C, 4 to 48h
d) Amberlyst-15, rt



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Flourat A.L. *et al.* *Green Chem.* **2015**, *17*, 404

Allais F. *et al.* WO 2015165957, **2015**

Bonneau G. *et al.* *Green Chemistry* **2018**, *20*, 2455

Allais F. *et al.*, G. Bonneau, A. A. M. Peru, A. L. Flourat WO 2018007764, **2018**

L. M. M. Mouterde, F. Allais*; J. D. Stewart* *Green Chem.* **2018**, *20* (24), 5528

J. D. Stewart, F. Allais, L. M. M. Mouterde WO 2018183706, **2018**

J. D. Stewart, F. Allais, L. M. M. Mouterde, WO2020095008A1 **2020**

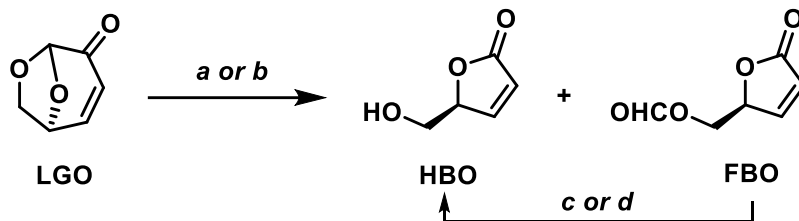
Chimie verte



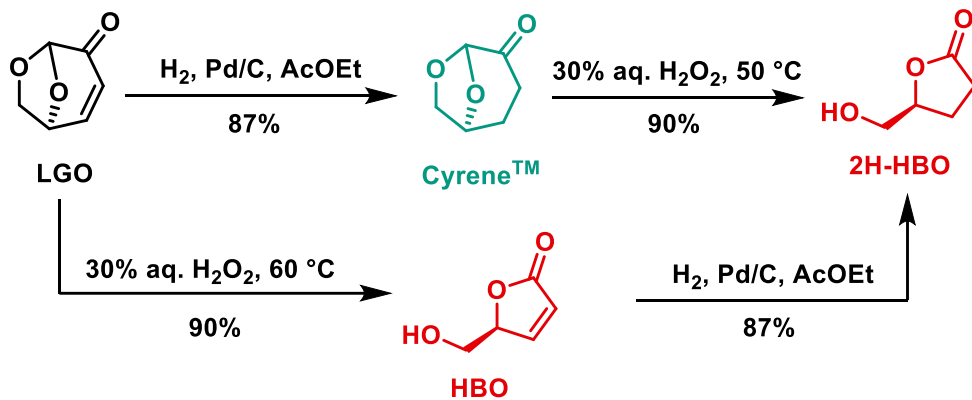
Biotechnologie



La Lévo-glucosénone



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Allais F. *et al.*, G. Bonneau, A. A. M. Peru, A. L. Flourat WO 2018007764, **2018**

L. M. M. Mouterde, F. Allais*; J. D. Stewart* *Green Chem.* **2018**, 20 (24), 5528

J. D. Stewart, F. Allais, L. M. M. Mouterde WO 2018183706, **2018**

J. D. Stewart, F. Allais, L. M. M. Mouterde, WO2020095008A1 **2020**

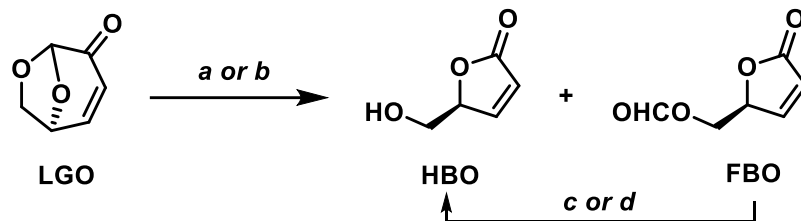
Chimie verte



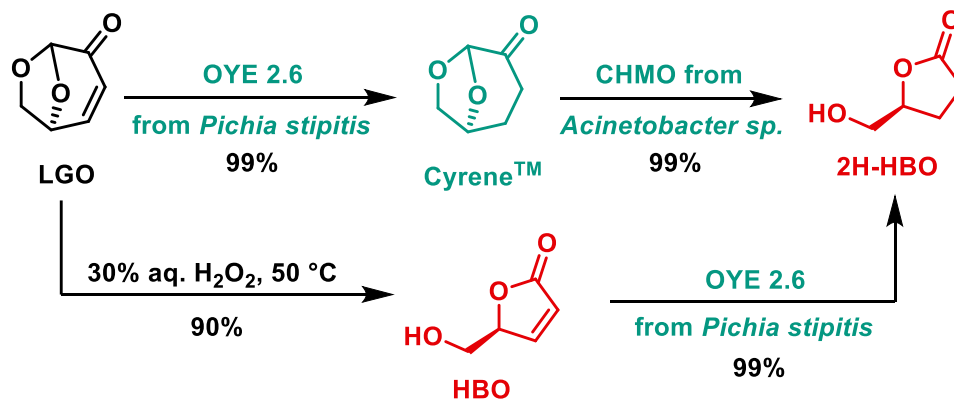
Biotechnologie



La Lévo-glucosénone



Koseki's procedure: a) MCPBA or AcOOH, Me₂S, 48h, rt
c) MeOH, HCl, 45 °C, overnight
Paris' procedure: b) Metal-Zeolite, 100 °C, 4 to 48h
d) Amberlyst-15, rt



URD ABI

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Flourat A.L. *et al.* *Green Chem.* **2015**, 17, 404

Allais F. *et al.* WO 2015165957, **2015**

Bonneau G. *et al.* *Green Chemistry* **2018**, 20, 2455

Allais F. *et al.*, G. Bonneau, A. A. M. Peru, A. L. Flourat WO 2018007764, **2018**

L. M. M. Mouterde, F. Allais*; J. D. Stewart* *Green Chem.* **2018**, 20 (24), 5528

J. D. Stewart, F. Allais, L. M. M. Mouterde WO 2018183706, **2018**

J. D. Stewart, F. Allais, L. M. M. Mouterde, WO2020095008A1 **2020**

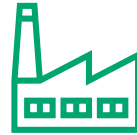


Forte demande de solvants biosourcés, non toxiques et renouvelables



Le projet

- Projet flagship BBI JU :
 - Projet Horizon 2020
 - 11 acteurs international et un budget de 23 M€
 - Timeline: **Octobre 2020 - Décembre 2024**



Construction d'usine

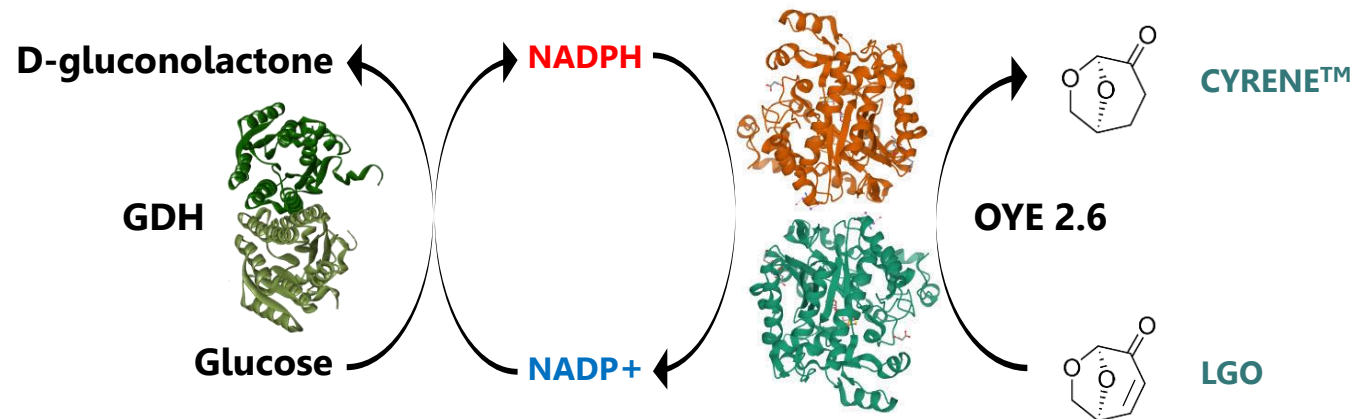
- Production de Cyrene™ *via* chimie verte
- Production de 1000+ tonnes/année
- A Saint-Avold, région Grand-Est, France



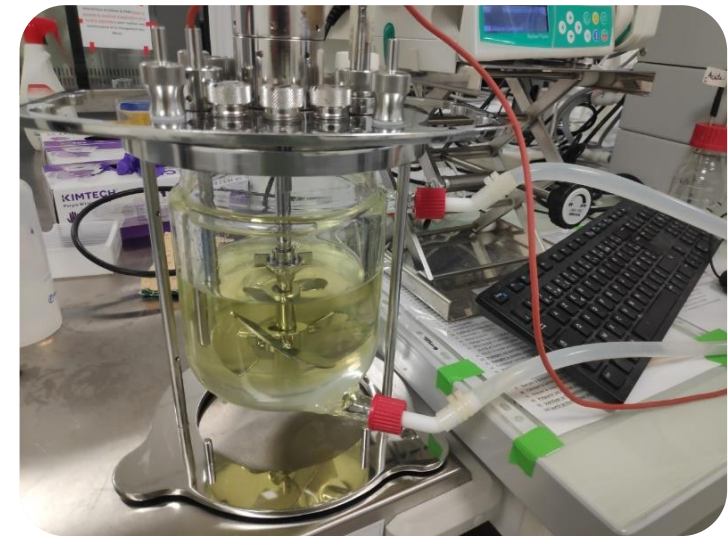
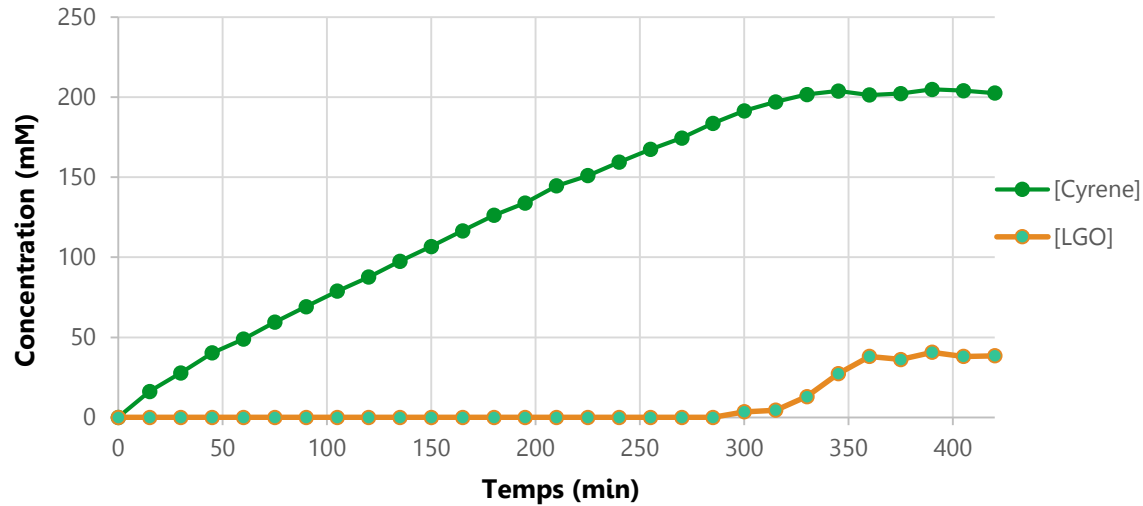
Acceptation du Cyrene™

- Education sur le procédé Cyrene™
- Nouveau procédé et technologies avec le Cyrene™
- Procédé de production alternative du Cyrene™

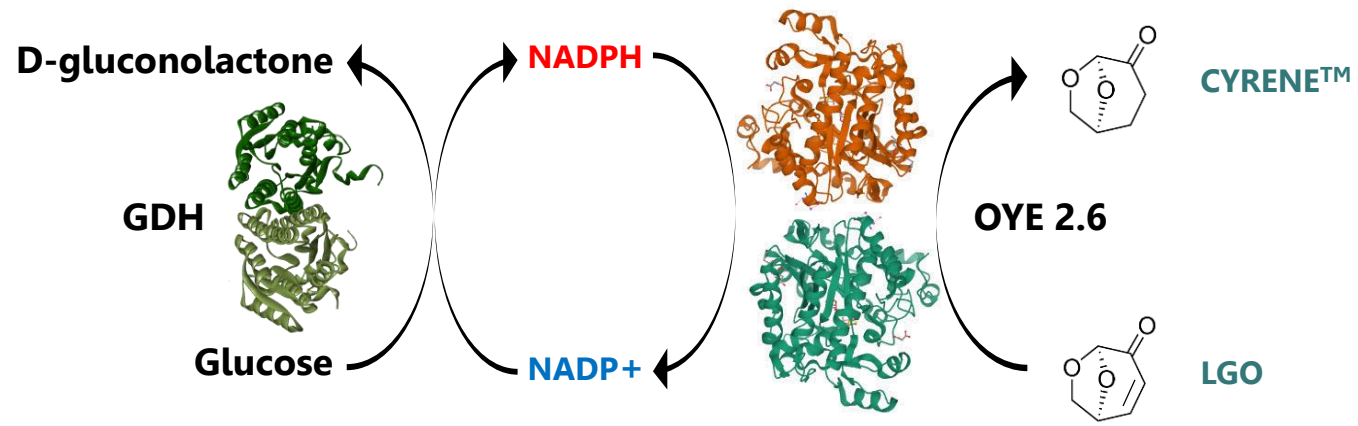
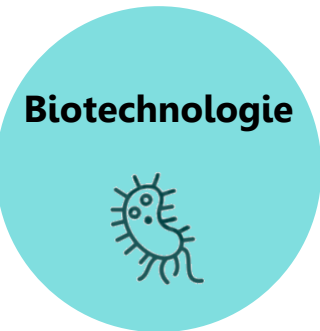




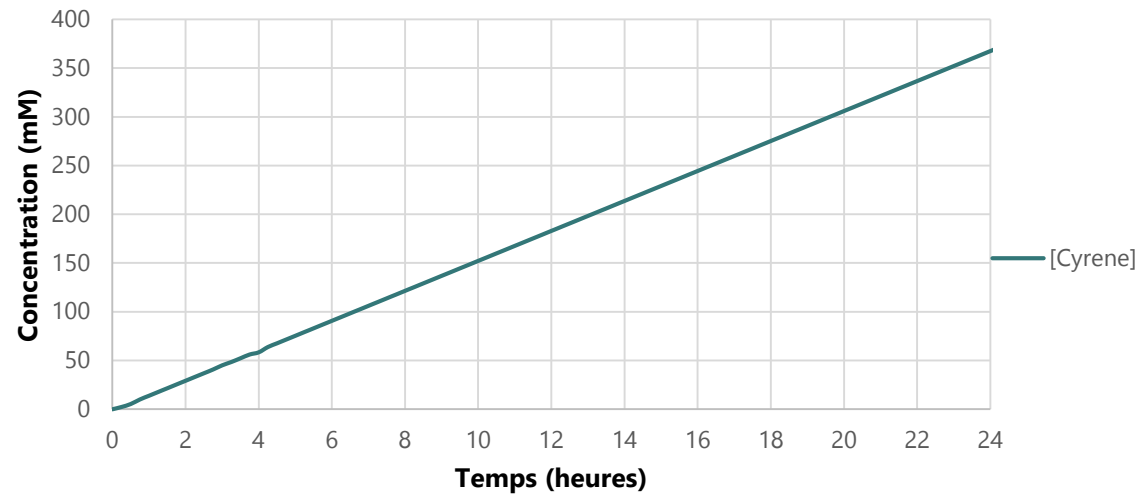
Concentration du Cyrene™ en fonction du temps



Production de **Cyrene™** en fed-batch 2,72 mL/h



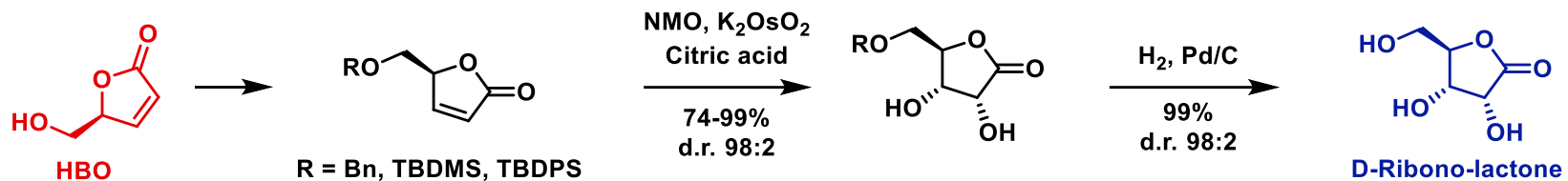
Concentration du Cyrene™ en fonction du temps



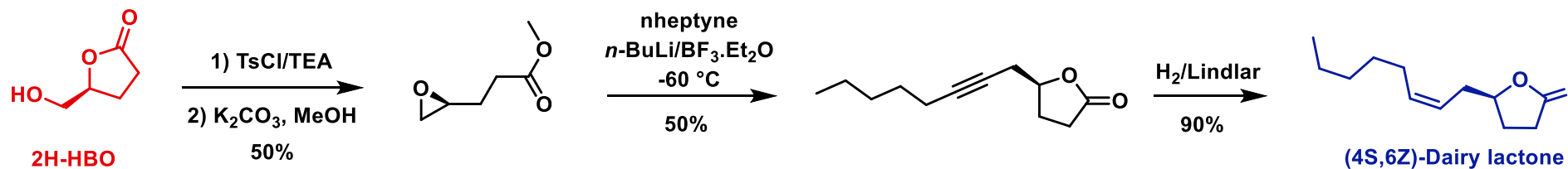
Production de **Cyrene™** en fed-batch 1 mL/h



La Lévo-glucosénone



Sucres rares



Arôme beurre



Conclusion

- **La vanilline, le syringaldéhyde et les acides p-hydroxycinnamiques** sont de précieux **building blocks biosourcés** issus de la **lignine**.
- **Des procédés (bio)chimiques durables** ont été conçus et optimisés pour la production de :
 - **Substituts non-toxiques au BPA, des monomères et polymères**
 - **Filtres UV biosourcés** possédant des **propriétés antioxydantes**
 - **Building blocks dérivés de la cellulose, solvants et composés chimique finis**
- **Des procédés (bio)chimiques durables** ont été montés à l'échelle du **multi-grammes** ou **kilogramme**.

Merci pour votre attention.

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September 28, 2023

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