One-Pot Syntheses of Biodegradable and Non-Ecotoxic Surfactants from Pectins and Algal Polysaccharides

Dr. Guillaume NOIRBENT

Guillaume.noirbent@ensc-rennes.fr

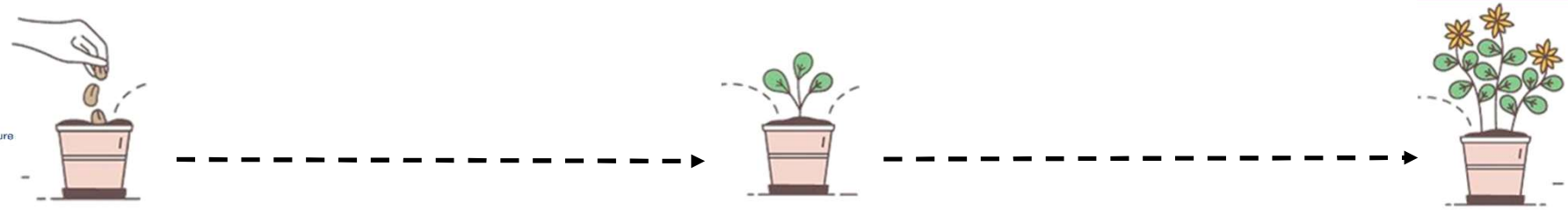
Ecole Nationale Supérieure de Chimie de Rennes

Surfact Green

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Université de Rennes

SurfactGreen & ENSCR



80's
Start of researches on biobased surfactants at ENSCR

2016
Creation of SurfactGreen

TODAY
≈ 40 years of common R&D on bio-based surfactants

Common goals

Development of bio-based surfactants

Physical and chemical characterisation

Formulation

SG: Awarded and Thriving

11 patent-pending

15 awards since 2016

2018 & 2019 : Innovation competition

2020 : Cleantech innovation competition (Shanghai)

2021 & 2023: E-Cosmet'Agora Formulation

2021 : Supplier Beauty Creators Awards

2022: Prix Pierre Potier

Which challenges for the surfactant industry?

Structures of surfactants

Non ionics: 50% Anionics: 40%

Cationics: 8% Amphoterics: 2%

Cosmetics

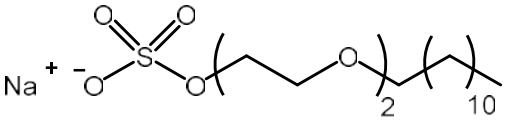
Detergence

Construction, bitumen

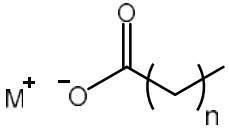
Few 100% biosourced surfactants (≈ 5% of the global market)…

…And fewer 100% cationic and anionic biosourced surfactants with high efficiency are on the market

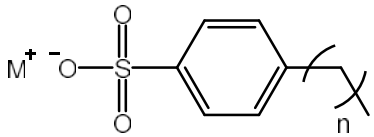
Anionic surfactants



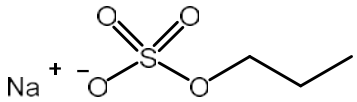
SLES : Sodium Lauryl Ether Sulfate



Fatty carboxylate



Alkyl benzene sulfonate



SCI : Sodium Cocoyl Isethionate

- Based on sulfate/ sulfonate / carboxylate groups
- Synthesis from harmfull reactants
- Controversed anionic surfactants, especially in cosmetic industry due to the skin irritation issue

How can we design new anionic surfactants ?

Challenges

- Reduce the use of toxic chemicals
- Favorise the use of green chemistry principles
- 100% bio-based surfactants
- Biodegradable and non-ecotoxic structures
- New properties/ functionalities
- High efficiency

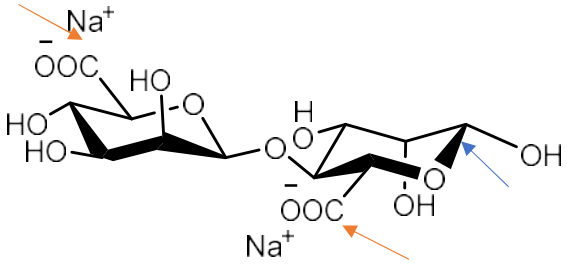
General procedure

Direct transformation of natural polysaccharides into anionic surfactants :

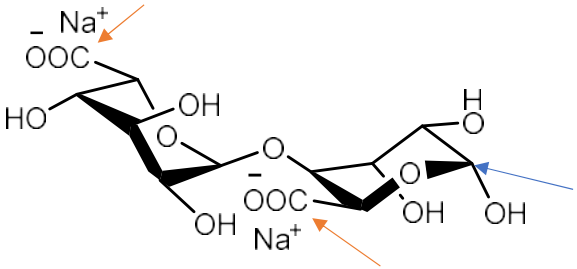
- One-pot and cascade mode process

Polysaccharides, sources of chemical diversity

Brown algae
Alginates

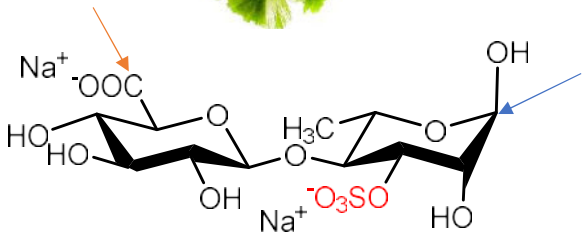


β-D-mannuronate

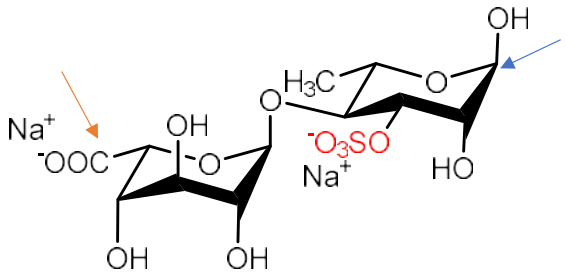


α-L-guluronate

Green algae
Ulvans



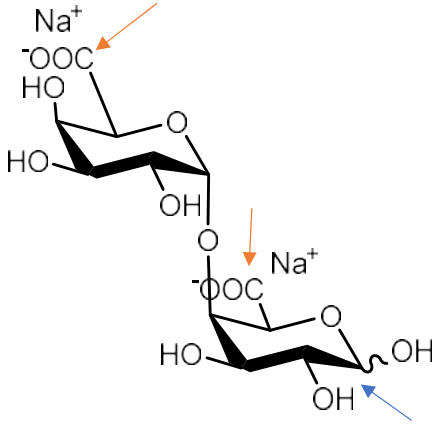
Type $A3_S$ ulvan monomer



Type $B3_S$ ulvan monomer

Agrobased wastes
Pectins

Citrus peel ***Sugar beet pulp***



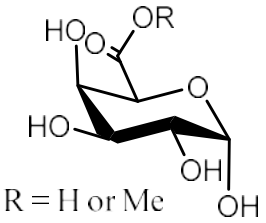
Pectin backbone
D-galacturonate

← Site for glycosylation with fatty alcohols

← Site for esterification or alkylation

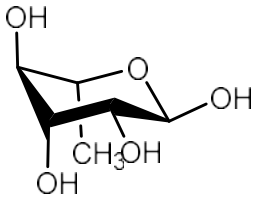
Example from pectin polysaccharide

Molar composition of pectin polysaccharide from citrus



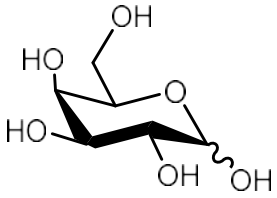
D-galacturonic acid (GalA)

79 mol%



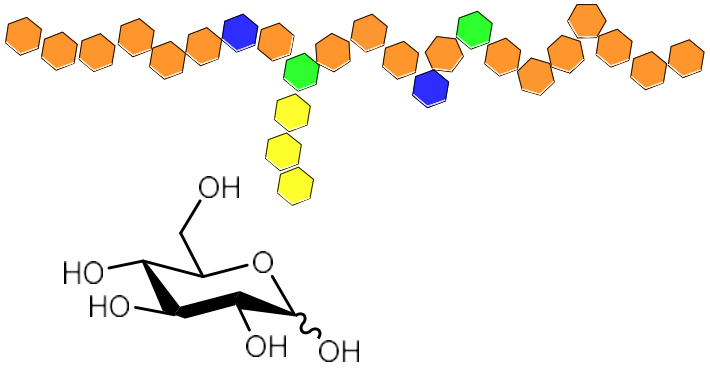
L-rhamnose

5 mol%



D-galactose

11 mol%



D-glucose

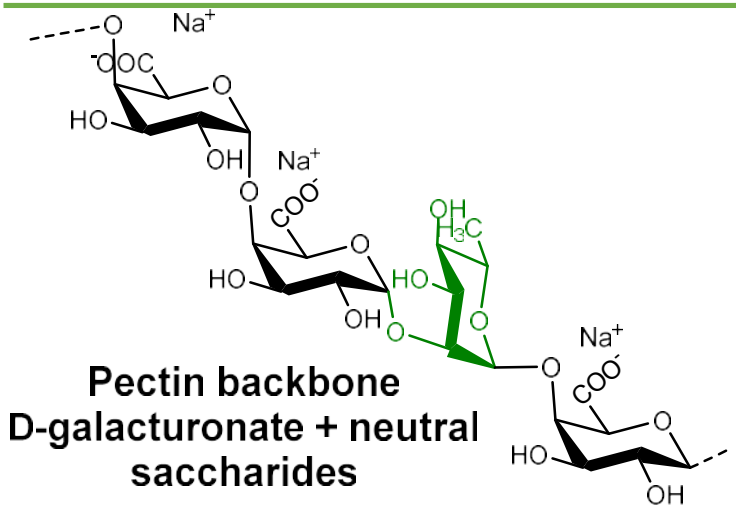
5 mol%

Characteritics of Pectin:

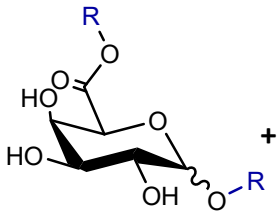
- **Mw: 381 kDa**
- **GalA: 67% (in mass percent)**
- **Degree of methyl esterified GalA: 30%**

Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

Example from pectin polysaccharide



Pectin backbone
D-galacturonate + neutral saccharides



+ Neutral alkylglycosides derivated from Gal*p*, Rha and Glc

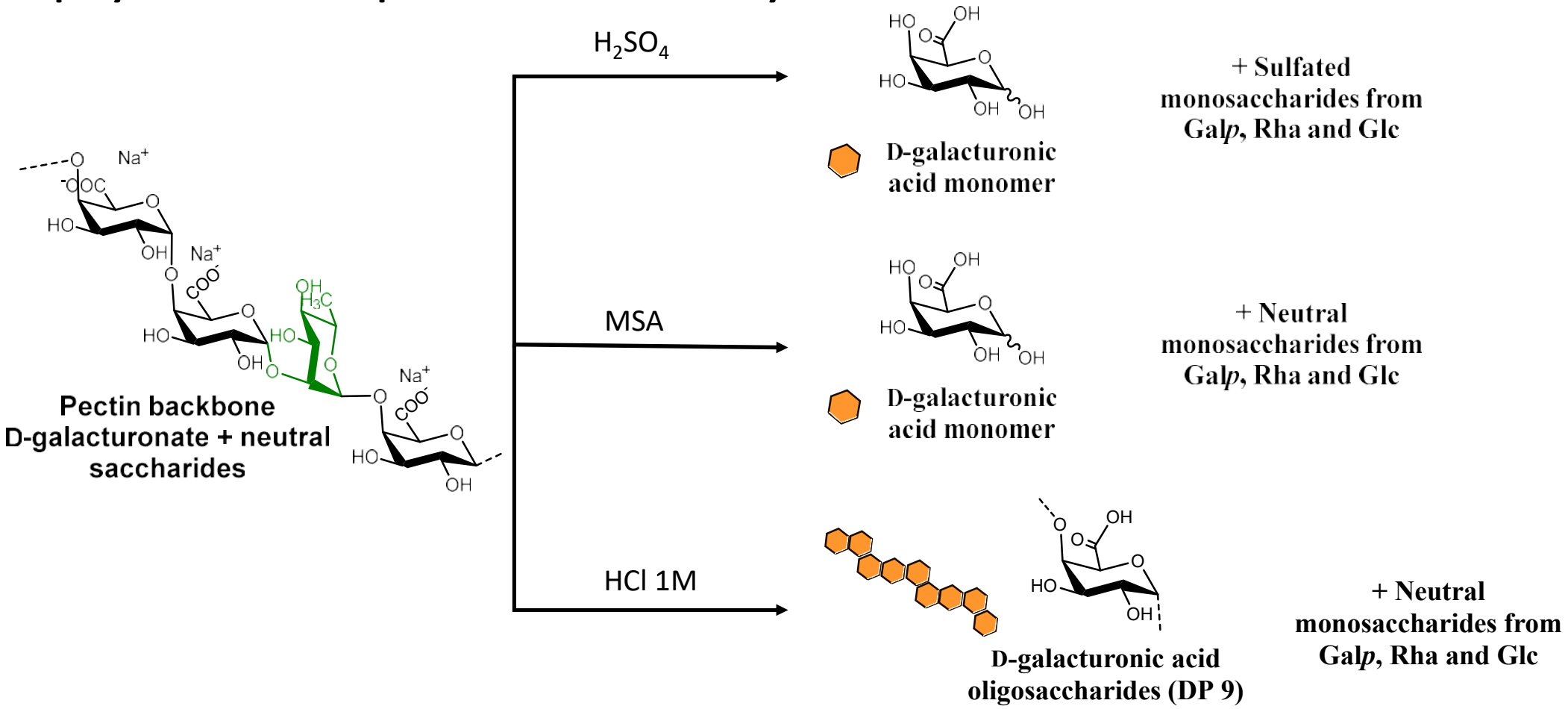
Alkyl-D-galactoside uronate

Depolymerisation step coupled with butanolysis → Transesterification/ Transglycosylation → Saponification step followed by an acidification (pH 2) → One-pot process: purification steps

Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

Example from pectin polysaccharide

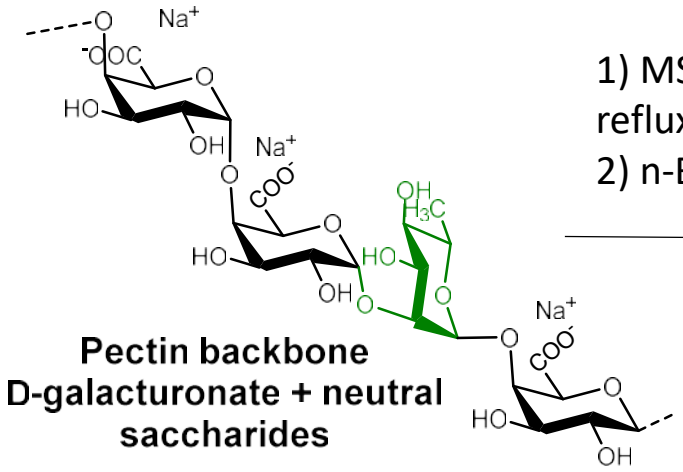
Depolymerisation step - Choice of acid catalyst



Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

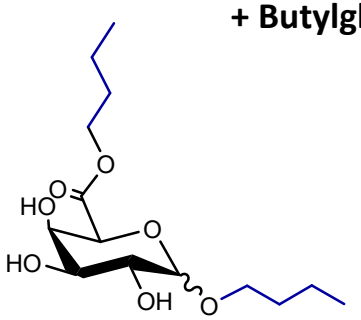
Example from pectin polysaccharide

Depolymerisation coupled with butanolysis



Pectin backbone
D-galacturonate + neutral saccharides

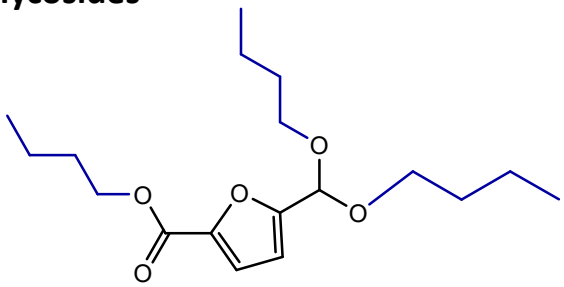
1) MSA (2.5 eq.), H_2O (n eq.), reflux, 5 h, 100°C
2) n-BuOH (100 eq), 80°C, 24 h



butyl-1-butoxy-D-galacturonate

n = 1000 y = 76%
n = 200, y = 21%

+ Butylglycosides

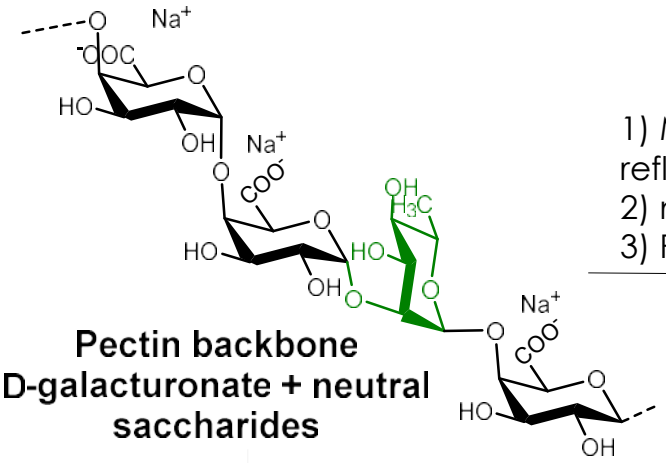


butyl-5-(dibutoxymethyl)-2-furanoate (BDMF)

n = 1000 y = 6%
n = 200, y = 1%

Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

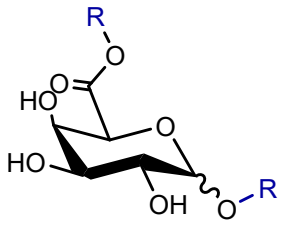
Example from pectin polysaccharide



Pectin backbone
D-galacturonate + neutral saccharides

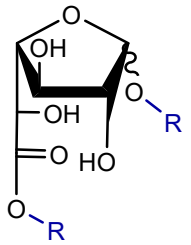
1) MSA (2.5 eq.), H_2O (n eq.), reflux, 5 h, 100°C
2) n-BuOH (100 eq), 80°C, 24 h
3) ROH (4 eq), 70°C, 10 mbar, 5 h

+ Neutral alkylglycosides derivated from Galp, Rha and Glu



alkyl-D-galactopyranosiduronate (Gal*p*)

R : $C_{12}H_{25}$ y=33%
R : $C_{18}H_{35}$ y=40%



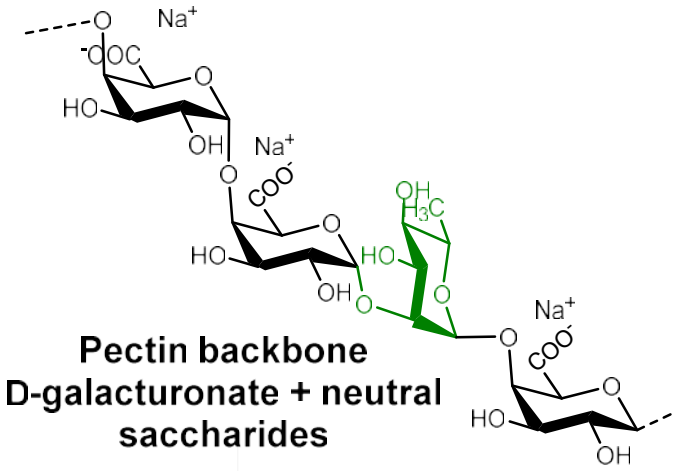
alkyl-D-galactofuranosiduronate (Gal*f*)

Depolymerisation step coupled with butanolysis → Transesterification/ Transglycosylation → Saponification step followed by an acidification (pH 2) → One-pot process: purification steps

76% **33-40%**

Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

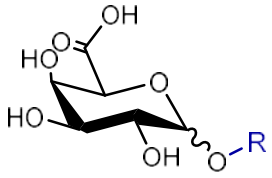
Example from pectin polysaccharide



Pectin backbone
D-galacturonate + neutral saccharides

1) MSA (2.5 eq.), H_2O (n eq.), reflux, 5 h, 100°C
2) n-BuOH (100 eq), 80°C, 24 h
3) R_1OH (4 eq), 70°C, 10 mbar, 5 h

4) 1N NaOH (3,6 eq), 12 h, 30 °C
5) HCl pH 2



Alkyl D-galactosiduronic acid

R : $C_{12}H_{25}$ y=37%
R : $C_{18}H_{35}$ y=42%

+ Neutral alkylglycosides derivated from Galp, Rha and Glu

Depolymerisation step coupled with butanolysis

76%

Transesterification/ Transglycosylation

33-40%

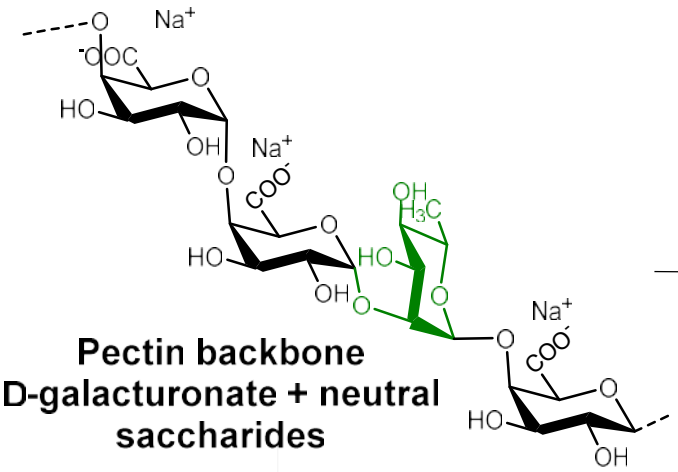
Saponification step followed by an acidification (pH 2)

37-42%

One-pot process: purification steps

Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

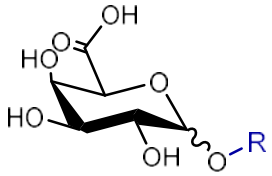
Example from pectin polysaccharide



Pectin backbone
D-galacturonate + neutral saccharides

1) MSA (2.5 eq.), H_2O (n eq.), reflux, 5 h, 100°C
2) n-BuOH (100 eq), 80°C, 24 h
3) R_1OH (4 eq), 70°C, 10 mbar, 5 h

4) 1N NaOH (3,6 eq), 12 h, 30 °C
5) HCl pH 2



Alkyl D-galactosiduronic acid

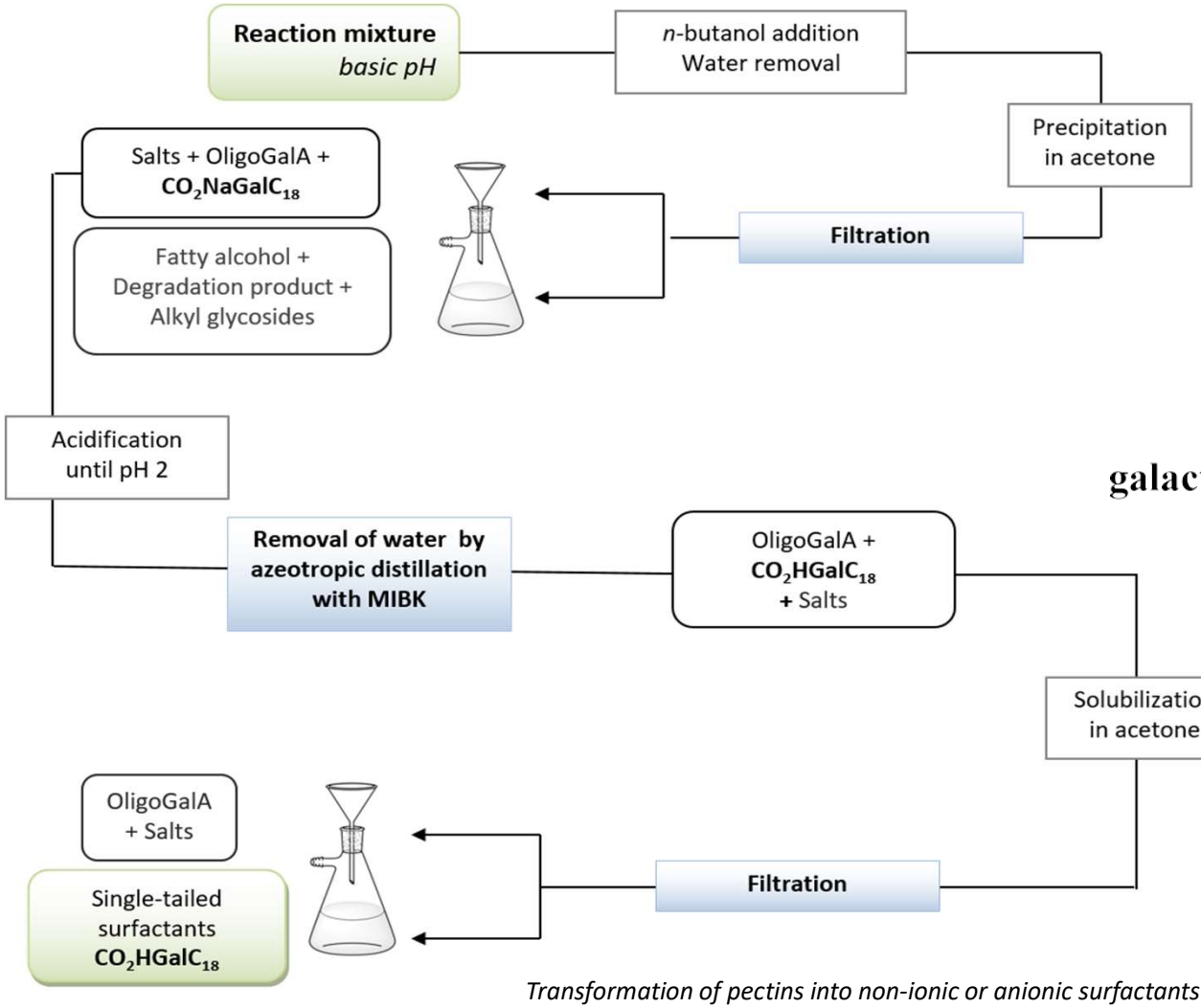
+ Neutral alkylglycosides derivated from Galp, Rha and Glu

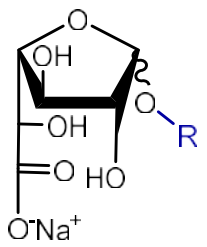
Depolymerisation step coupled with butanolysis → Transesterification/ Transglycosylation → Saponification step followed by an acidification (pH 2) → One-pot process : Purification steps

76% **33-40%** **37-42%**

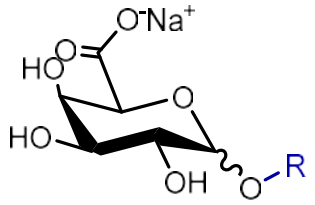
Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

Example from pectin polysaccharide





D-alkyl galactofuranosiduronates (Gal*f*)



D-alkyl galactopyranosiduronates (Gal*p*)

yield = 62 %; purity > 95%

Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, ***Molecules, 2021****, 26* 1956.

Example from pectin polysaccharide

Sugar beet pulp
Pectins + Non-ionic glycosides
(L-arabinose & D-glucose)

?

Mix of ionic & non-ionic surfactants

Depolymerisation step coupled with butanolysis → Transesterification/ Transglycosylation → Saponification step followed by an acidification (pH 2) → Purification steps (distillation or filtration)

Method for obtaining surfactant compositions from raw plant materials, WO 2022/013500, ***2022***

Can we start from sugar beet pulp ?

Dried Sugar Beet Pulp — **100 g**

MSA 70%: 30 g
***n*-BuOH : 140 mL**
120-135°C
7 h

Filtration → Residues and waste from beet pulp

Butylated sugars + *n*-BuOH + Salts

C8-OH : 200 mL
70°C
25 mbar
5-7 h
→ Recovering of *n*-BuOH and H_2O

Octylated sugars + Octanol + Salts

5N NaOH: 20 mL
65°C, 50 mbar, 1-2 h

H_2SO_4 95%: 3 mL

Precipitation of salts

Filtration → Removal of salts

Octylated sugars + Octanol

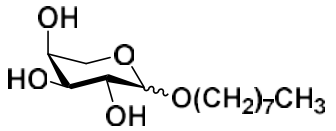
→ Octanol recovery

Molecular distillation

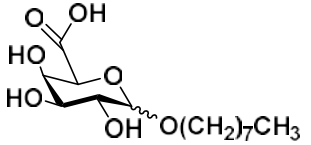
Final Product — **Mass = 41g**

Surfactant composition from SBP:

- Organic matter (76 mass%)
- Water (11 mass%)
- Ash (13 mass%)



42 molar %



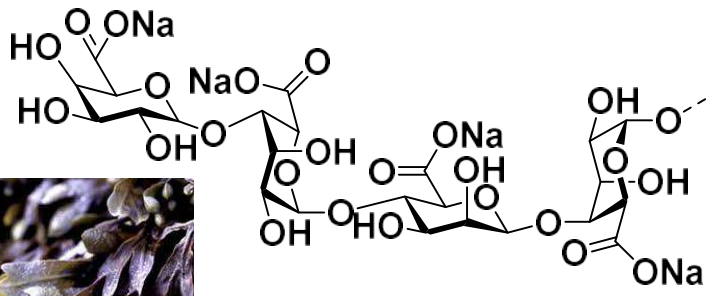
38 molar %

+ other octyl glycosides (gluco, rhamno, galacto,..)

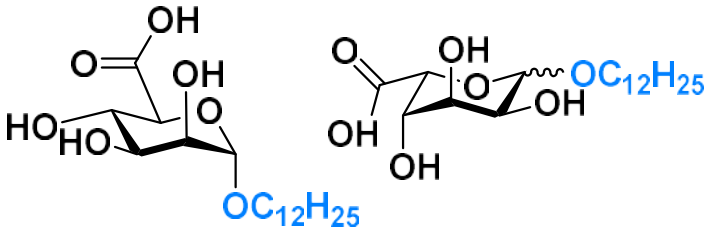
20 molar %

Method for obtaining surfactant compositions from raw plant materials, WO 2022/013500

Extension to purified alginate polysaccharides



1) H_2O, MSA (2.5 eq.) , reflux, 8 h
2) *n*-BuOH (150 eq.), reflux, 15 h
3) $C_{12}H_{25}OH$ (4 eq.), 70°C, 5 mbar, 1.5 h
4) 0.4N NaOH (2.8 eq.)
5) Purification based on filtration and distillation steps



yield = 43%

From alginate extracted polysaccharides

Depolymerisation step coupled with butanolysis → Transesterification/ Transglycosylation → Saponification step followed by an acidification (pH 2) → Purification steps (distillation or filtration)

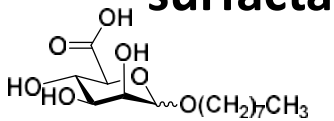
Process for preparing compositions comprising alkyl(alkyl-glucoside)uronates, said compositions and use thereof as a surfactant, WO 2017/098175

Anionic Surfactants from Milled Dried Seaweeds (MDS)

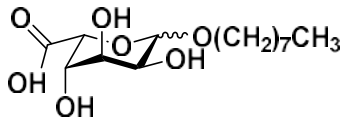
Milled Dried Seaweed
Ascophyllum nodosum
Alginate + Fucose

?

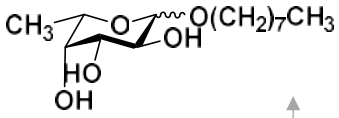
Mix of ionic & non-ionic surfactants



30 molar %



25 molar %



35 molar %

Mass = 24 g

Depolymerisation step coupled with butanolysis → Transesterification/ Transglycosylation → Saponification step followed by an acidification (pH 2) → Purification steps (distillation or filtration)

Method for obtaining surfactant compositions from raw plant materials, WO 2022/013500, ***2022***

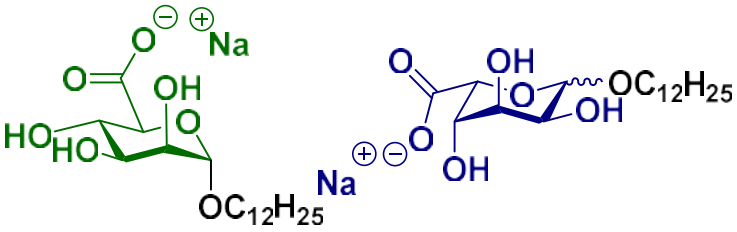
Properties evaluation

Reduction of surface tensions
values ≤ 30 mN/m at concentrations 10-15 times lower than other petrosourced surfactants (SDS and SLES)

Good sensory properties
rich, non-greasy touch

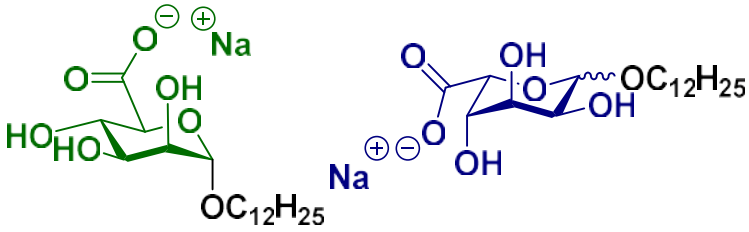
OCDE Tests :
Readily Biodegradable
Non eco-toxic (algae, daphnia, fish)

Foaming agent



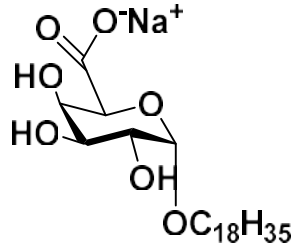
Dodecyl-D-mannuronate
Dodecyl-L-guluronate

Degreaser



Dodecyl-D-mannuronate
Dodecyl-L-guluronate

Emulsifier

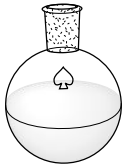


Oleyl D-galacturonate

Conclusion



100% biobased novel anionic surfactants



One-pot process

Use of green chemistry principles

Good physico-chemical properties

Biodegradable

Non-ecotoxic

Scale-up and cost investigations

Application in formulations in detergency or cosmetic industries

Interested in these new technologies?

Contacts:
Pr. Thierry BENVEGNU, thierry.benvegnu@ensc-rennes.fr
SurfactGreen, surfactgreen@surfactgreen.com

Thank you for your attention

Aknowledgements

Surfact Green, Ecole Nationale Supérieure de Chimie de Rennes, Institut des Sciences Chimiques de Rennes UMR CNRS 6226, Ille & Vilaine Le Département, SynNanoVect, Région Bretagne, bpifrance, ADEME Agence de la Transition Écologique

Contributing authors

M. Benoît, T. Benvegnu, C. Boyère, F. Galle, J-P. Guégan, Y. Le-Long, H. Mawlawi, D. Milliaseau, F. Pessel, L. Renault, X. Roussel, N. Sari-Chmayssem, S. Taha