Tensioactifs Biosourcés Verts/Bleus et Molécules 'Plateforme' : Vers de Nouveaux Synthons et de Nouvelles Fonctionnalités en Formulation

Thierry BENVEGNU – Les mardis de la Chimie Durable – 25 Mai 2021

thierry.benvegnu@ensc-rennes.fr

Ecole Nationale Supérieure de Chimie de Rennes

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Surfact Green

thierry.benvegnu@surfactgreen.com

CORINT : Chimie Organique & Interfaces

UNIVERSITÉ DE RENNES 1 · CNRS · Ecole Nationale Supérieure de Chimie de Rennes · INSA Institut National des Sciences Appliquées Rennes

The Laboratory at the ENSC Rennes

- Expertise in **Green/Sustainable Chemistry** for the production of **eco-friendly surfactants from biomass**
- Expertise in **physico-chemistry** and **surfactant formulation**

Original Renewable Raw Materials

↓ Design

↓ Production Process

New Biosourced Surfactants

↓

Application Fields

Targeted Functionnality and Market

Selection of Renewable Raw Materials

↓ Design

↓ Production Process

New Biosourced Surfactants

Creation of the Surfact'Green Business Unit in 2011 at the ENSCR (Pr. T. Benvegnu)

Contact : Xavier Roussel

Chief Executive Officer

www.surfactgreen.com

SurfactGreen received the innovation trophy by Bpifrance

- Founded in **2016**
- **12 employees**, including 8 newcomers in 2018-2021
- **11 patents** from ENSCR and since 2016
- Winner of the **French Innovation Contest by Bpifrance** in 2018 and 2019, Winner of the **Shanghai Cleantech, Innovation Booster – SCPI+** Contest in 2020, 3rd **Formulation Award of e-cosmet'Agora 2021**

SurfactGreen : Winner of the Shanghai Cleantech Innovation Booster – SCIP + 2020 Contest !

- SurfactGreen develops, produces, formulates and commercializes **New Efficient Ionic Surfactants up to 100 % bio-based** produced through **Green and Blue Chemistry**.

- SurfactGreen products are **easily biodegradable** patented surfactants, offering **very low toxicity levels** for humans and the environment

Challenges and Opportunities for Green Surfactants

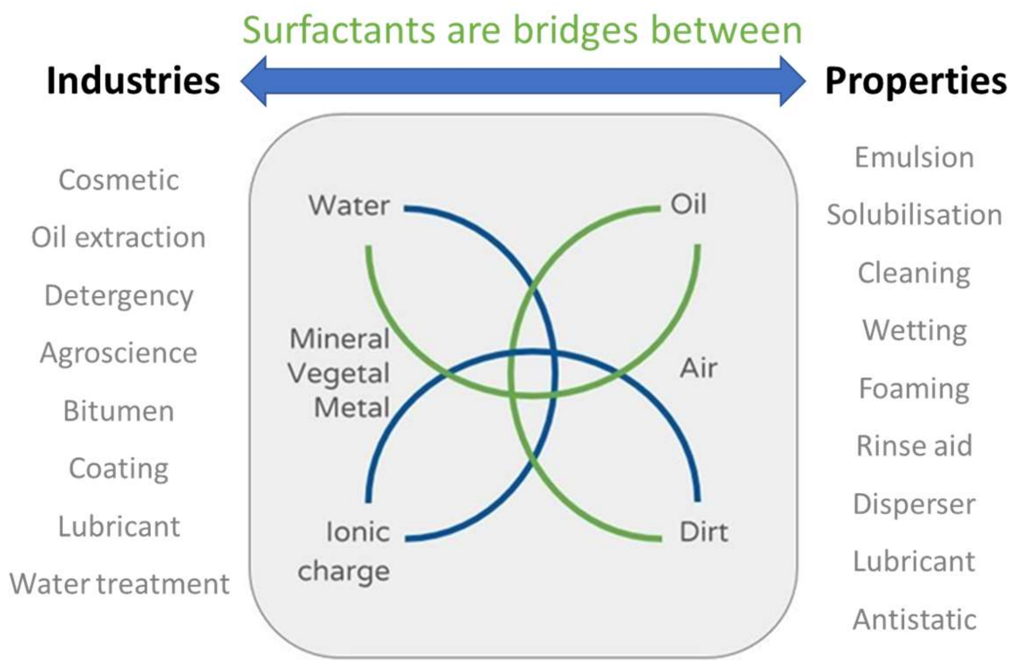
Opportunities

- Availability, variability and flexibility of renewable raw materials
- New processes and synthesis routes
- New functionalities in formulation
- Surfactant synergy and multifunctional abilities
- Consumer awareness towards safer and environmentally friendly ingredients
- Legislation that enforces the use of safer and environmentally friendly products

Challenges

- Sustainable way of sourcing them
- Price instability of the resources
- Optimisation of processes to fit the new raw materials
- High cost for new investments
- Consumers not willing to pay much for greener products
- Less competitive performance of greener surfactants

The surfactant market



2019: 39 Billion € Global Market

2024: 46 Billion € Global Market

On this market:

Non ionics: 50% **Anionics**: 40%

Cationics: 8% **Amphoterics**: 2%

100% Biosourced surfactants now represent 5-10% of the global surfactant market

Very few 100% biosourced cationic and anionic surfactants with high efficiency are on the market

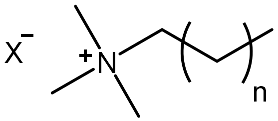
Design, synthesis and evaluation of biosourced, biodegradable, poorly/no eco-toxic high-performance surfactant

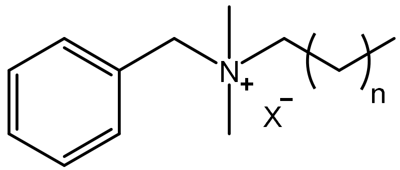
For many application segments of biosourced surfactants: cosmetics, detergents, oil extraction, agrochemicals, construction, bitumen, lubricants,...

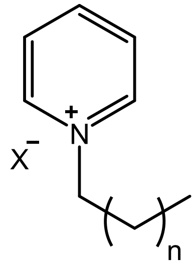
Cationic Surfactants

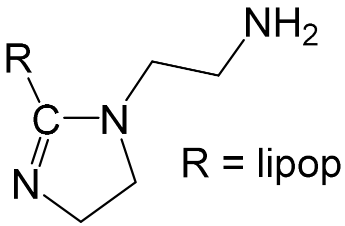
- 8% of the world's surfactant production

  - **Examples**









R = lipophilic chain

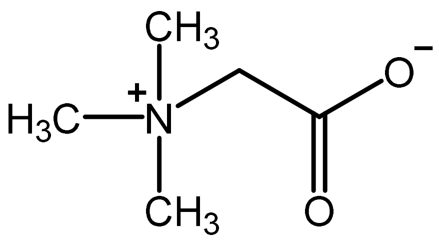
$R(NHCH_2CH_2CH_2)xNH_2$

R = lipophilic chain

  - **Problems**
    - Irritants
    - Low biodegradability
    - High eco-toxicity

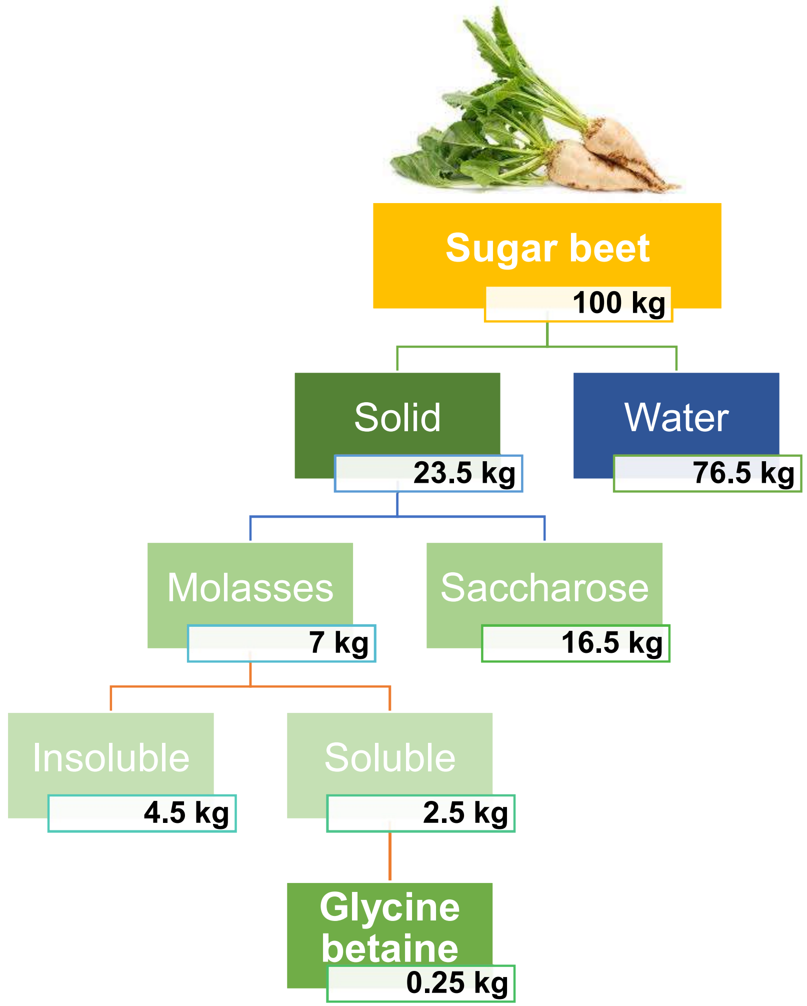
Biosourced cationic surfactants

- Sugar beet glycine betaine



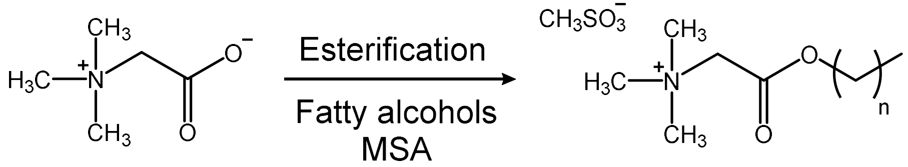
Advantages

- By-product of the sugar industry
- Available in abundance
- Low added value in animal nutrition
- Coupling reaction with fatty chains via the carboxylate function



Cationic surfactants based on by-products of the sugar industry: Two families with different properties

- **Esters: GBE.** Stable in acidic pH, readily biodegradable, reduced eco-toxicity compared to petro-sourced surfactants

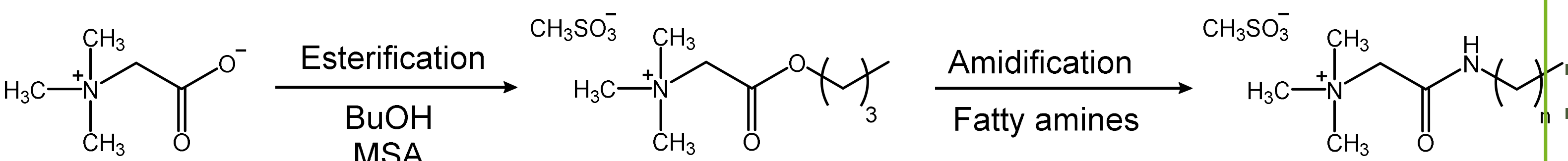


Glycine betaine

- **E factor** < 0.5 (Kg waste per Kg product)
- **AE** (Atom Economy) = 95%
- Solvent-free, use of renewable raw materials and/or biodegradable reagents

Note that GBEs are surfactants under the desired conditions of use. In the natural environment, products lose their surface-active properties

- **Amides: GBA.** Stable at all pH levels, readily biodegradable, reduced eco-toxicity compared to petro-sourced surfactants



Glycine betaine

- **E factor** < 0.5 (Kg waste per Kg product)
- **AE** (Atom Economy) = 80%
- Use of renewable raw materials, recyclable BuOH, and/or biodegradable reagents

Note that GBAs have a dual chemical function: quaternary ammonium and amide, which gives them specific properties

Glycine betaine as a renewable raw material to "greener" new cationic surfactants, *Green Chem.* ***2008****, 10*, 310;
FR2869913, **WO** 200512129, **US** 20070197420, **2005**.

Surfactants for Personal Care named CosmeGreen™

Nature friendly

Readily Biodegradable
No Labelling
Vegan and Cruelty-Free
Doesn't Compete with Human Food Chain
Non-OGM

MADE IN FRANCE

Green chemistry

One-Pot Process, No Solvent
Preservative-free
Sulfate-Free
Palm-Free
100% derived from Renewable Feedstock Sources

Verified by ECOCERT
COSMOS APPROVED

- **CosmeGreen ES1822+, 100% bio-sourced conditioning agent**

CosmeGreen ES1822+ is a 100% biosourced, cationic surfactant system with superior smoothing, strengthening, color retention and detangling benefits.

- **CosmeGreen MS1822, 99% bio-sourced conditioning agent**

CosmeGreen MS1822 is a 99% biosourced, cationic surfactant system with conditioning and detangling benefits.

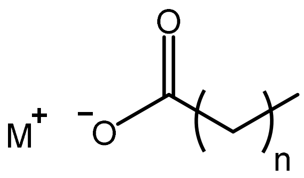
Hair Conditioning Solids
Deep Treatment Masks
Rinse-Out Conditioners

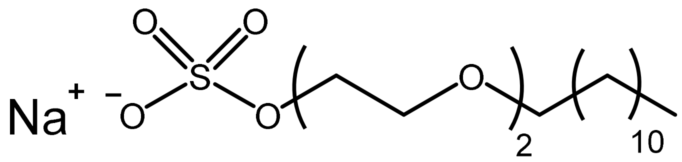
Conditioners
Solid Make Up Removers
Sun Care

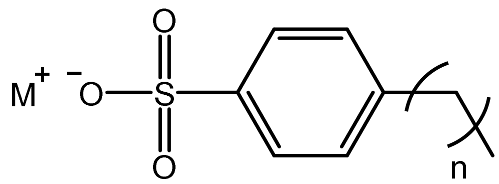
https://www.surfactgreen.com/fr/produits/cosmegreen-tensioactifs-biosources-pour-soins-corporels/

Anionic Surfactants

- 40% of the world's surfactant production
  - **Examples**





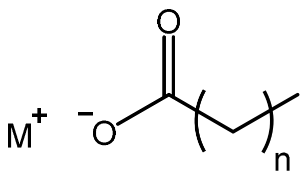


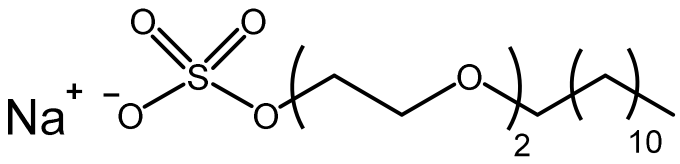
- **Problems**

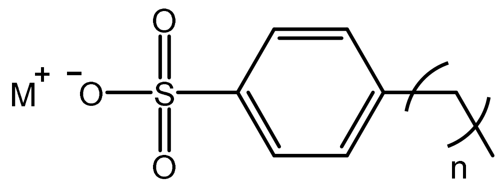
- Irritation
- Eco-toxicity

Anionic Surfactants

- 40% of the world's surfactant production
  - **Examples**







Direct Transformation of Natural Polysaccharides into Anionic Surfactants :

- **One-pot and Cascade Mode Process**
- **Biomass-Agnostic**
- **Towards Sugar- or Furan-Based Surfactants**

• Sugar-derived Anionic Surfactants

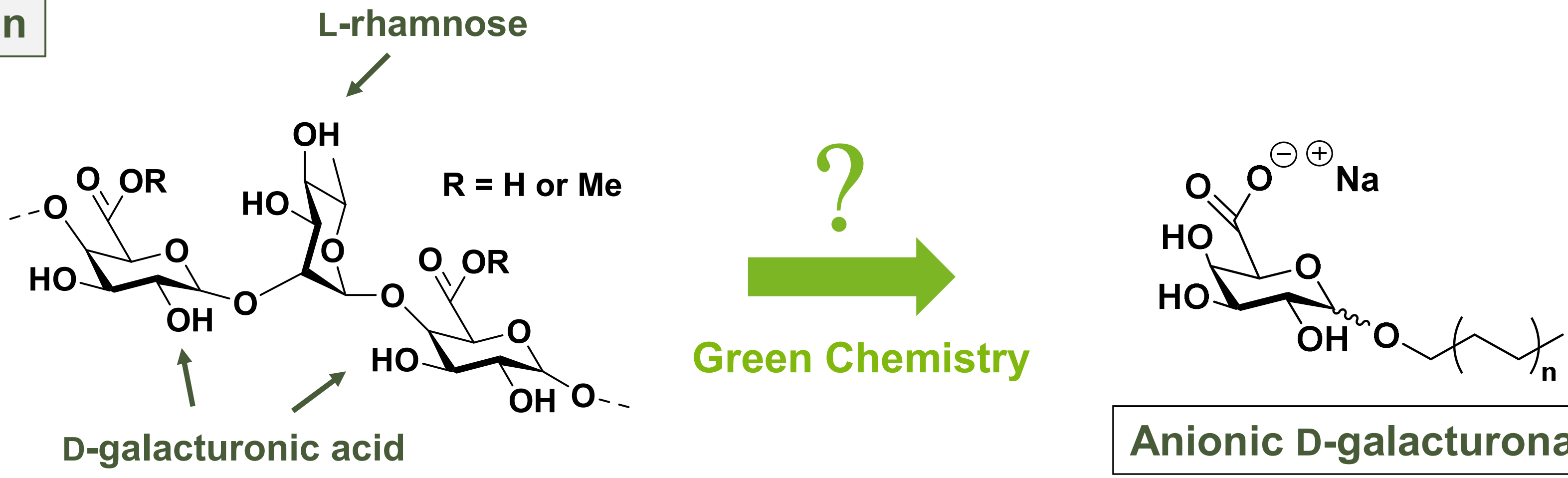
- Access to carboxylate-containing surfactants from natural polysaccharides incorporating the anionic functionality

• Advantages

- Avoid the use of toxic chemicals for the controlled introduction of carboxylate units
- 100% Bio-based surfactants "sulfate-free" and "ethylene oxide-free"

Anionic Surfactants from Pectins

Pectin

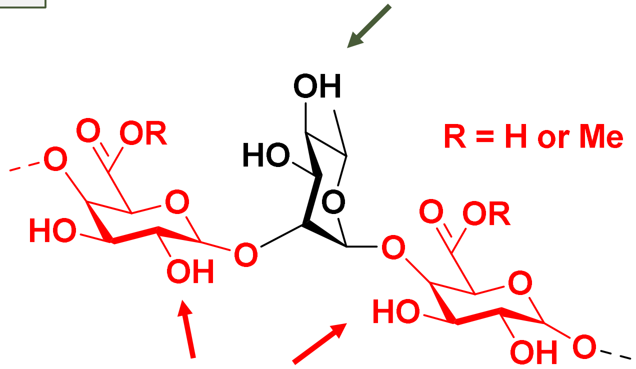


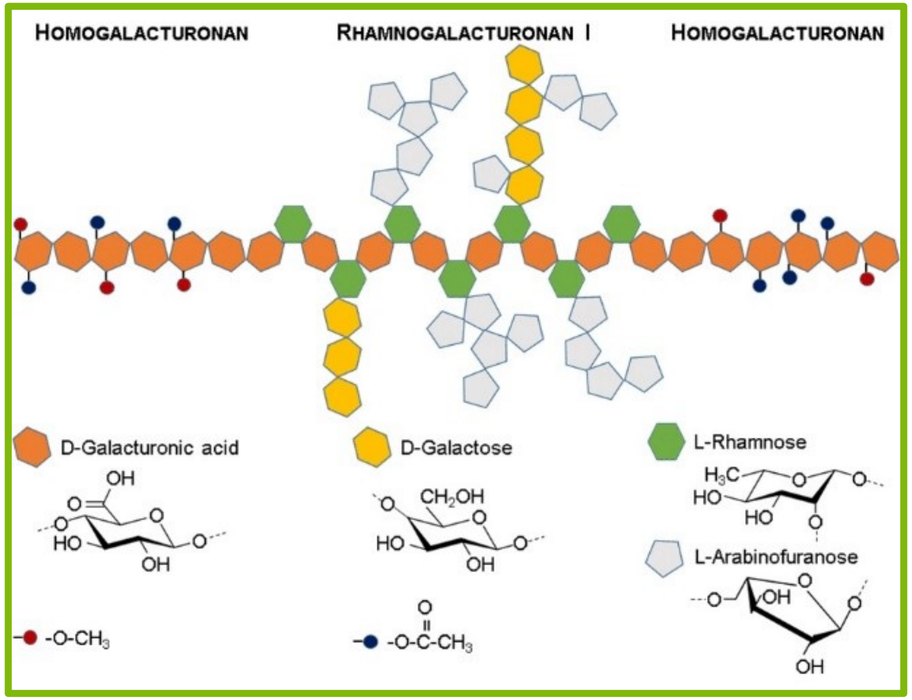
Anionic D-galacturonate surfactants

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

Anionic Surfactants from Pectins

Pectin





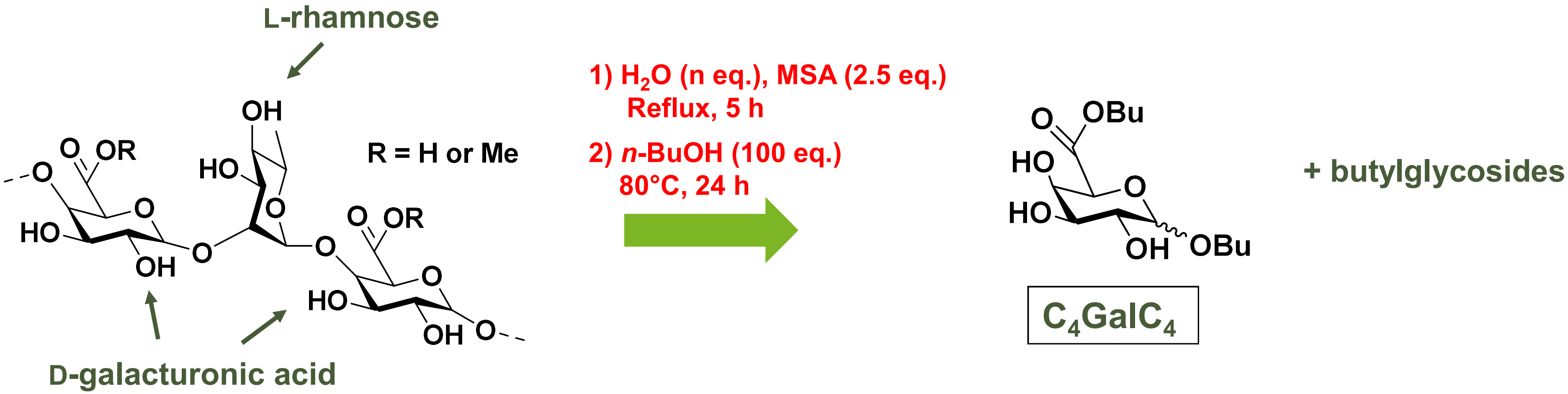
Characteritics of Pectin from Lemon Peel (Cargill):

- Mw: 381 kDa
- GalA: 67% (in mass percent)
- Degree of methyl esterified GalA: 30%
- Gal: 10%; Rha : 4%; Glc: 3% (in mass percent)

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

Anionic Surfactants from Pectins

Hydrolysis / Butanolysis



n = 1000 eq. ; Yield: 76%
n = 200 eq. ; Yield: 21%

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

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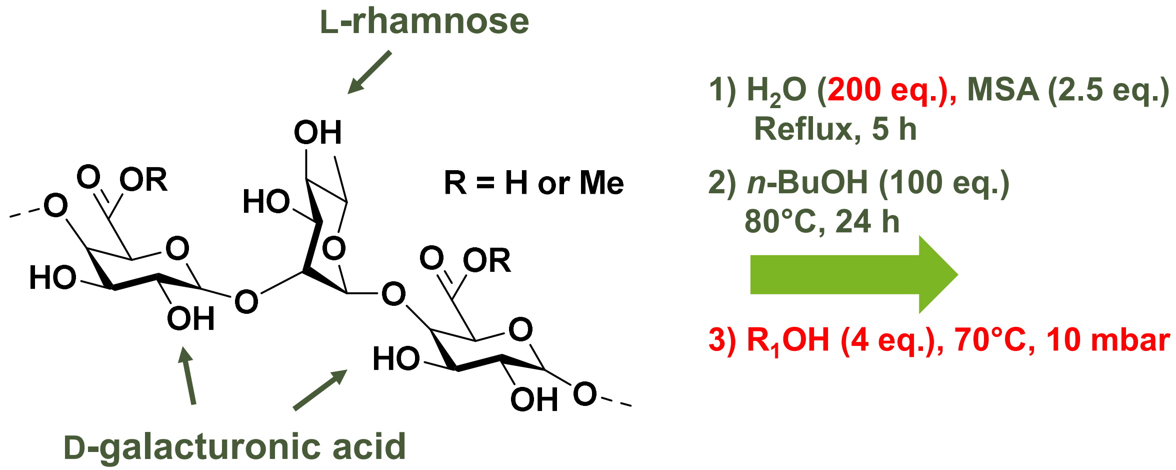
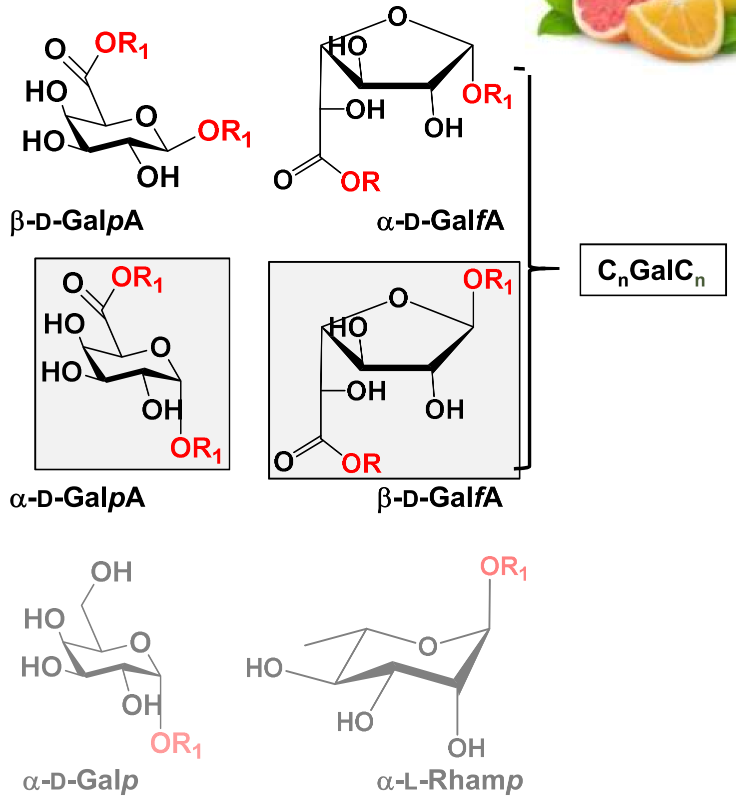
Anionic Surfactants from Pectins

Hydrolysis / Butanolysis / Transesterification / Transacetalisation



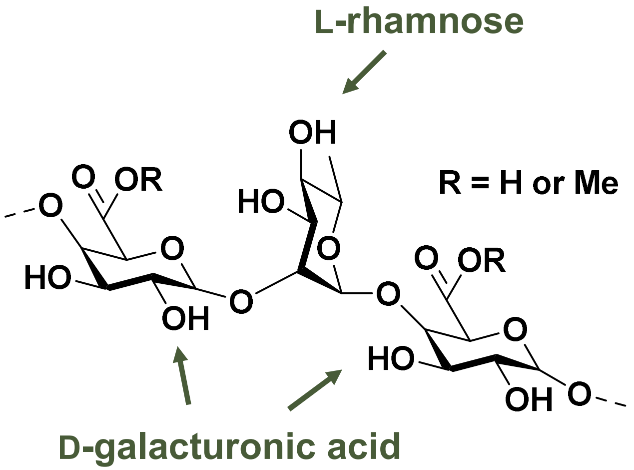


C_nGalC_n
$R_1 = C_{12}H_{25}$: Yield = 33%
$R_1 = C_{18}H_{35}$: Yield = 40%

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

Anionic Surfactants from Pectins

Hydrolysis / Butanolysis / Transesterification / Transacetalisation / Saponification

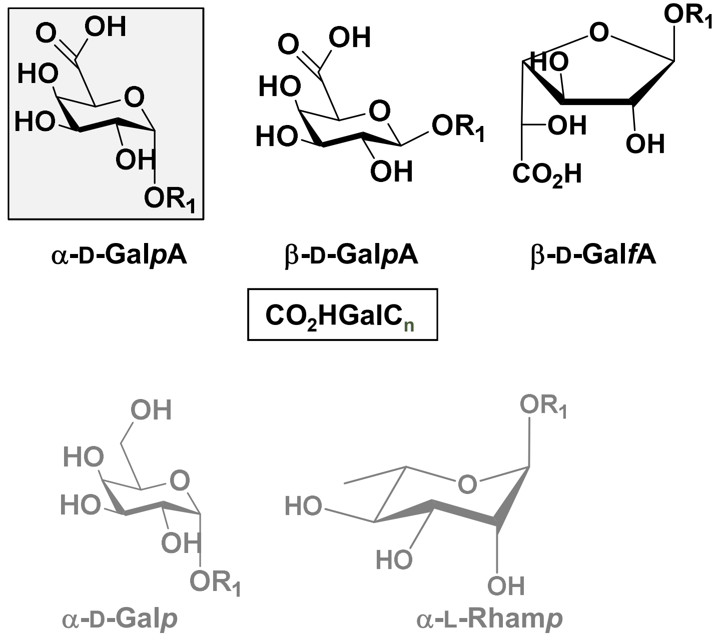


1) H_2O (200 eq.), MSA (2.5 eq.) Reflux, 5 h

2) *n*-BuOH (100 eq.) 80°C, 24 h

3) R_1OH (4 eq.), 70°C, 10 mbar

4) 1N NaOH (3.6 eq.), then 4N HCl (pH = 2)

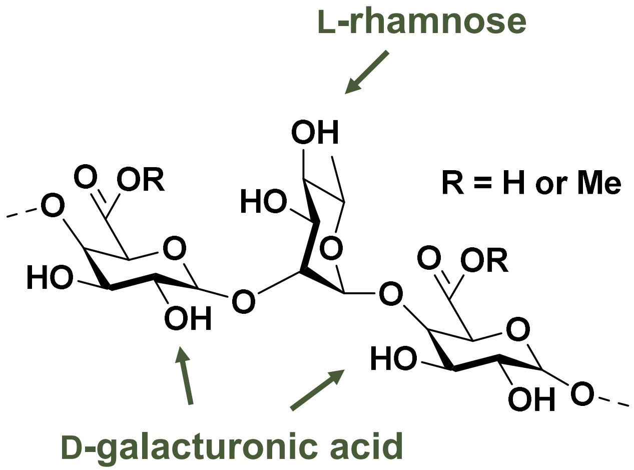


CO_2HGalC_n
$R_1 = C_{12}H_{25}$: Yield = 37%
$R_1 = C_{18}H_{35}$: Yield = 42%

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

Anionic Surfactants from Pectins

Hydrolysis / Butanolysis / Transesterification / Transacetalisation / Saponification / Post-reaction Treatment



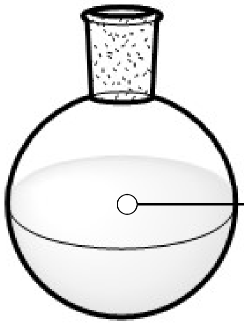
1) H_2O (200 eq.), MSA (2.5 eq.)
   Reflux, 5 h
2) *n*-BuOH (100 eq.)
   80°C, 24 h

3) $C_{18}H_{35}OH$ (4 eq.), 70°C, 10 mbar
4) 1N NaOH (3.6 eq.)
5) Purification based on filtration and distillation steps

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

Anionic Surfactants from Pectins

Reaction Mixture → *n*-butanol addition Water removal → Precipitation in acetone → Filtration



Basic pH

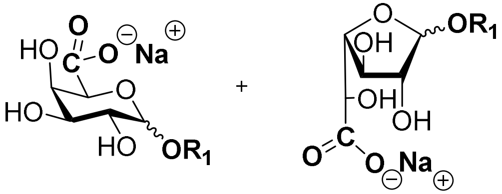
Degradation products

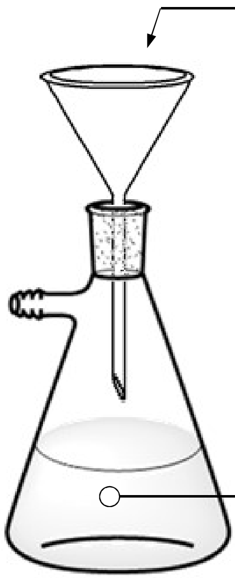
Fatty alcohol

Alkyl glycosides

Salts

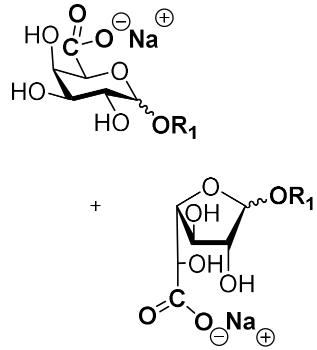
Oligosaccharides





Salts

Oligosaccharides



Degradation products

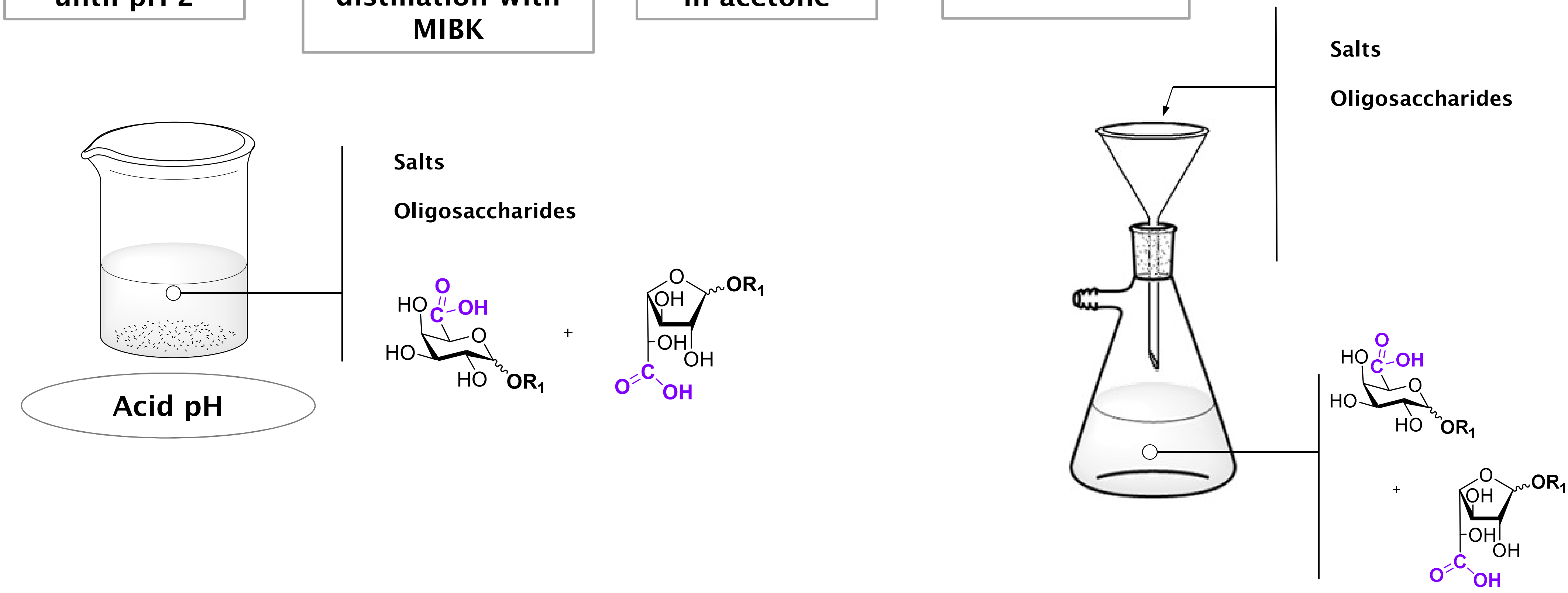
Fatty alcohol

Alkyl glycosides

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

Anionic Surfactants from Pectins

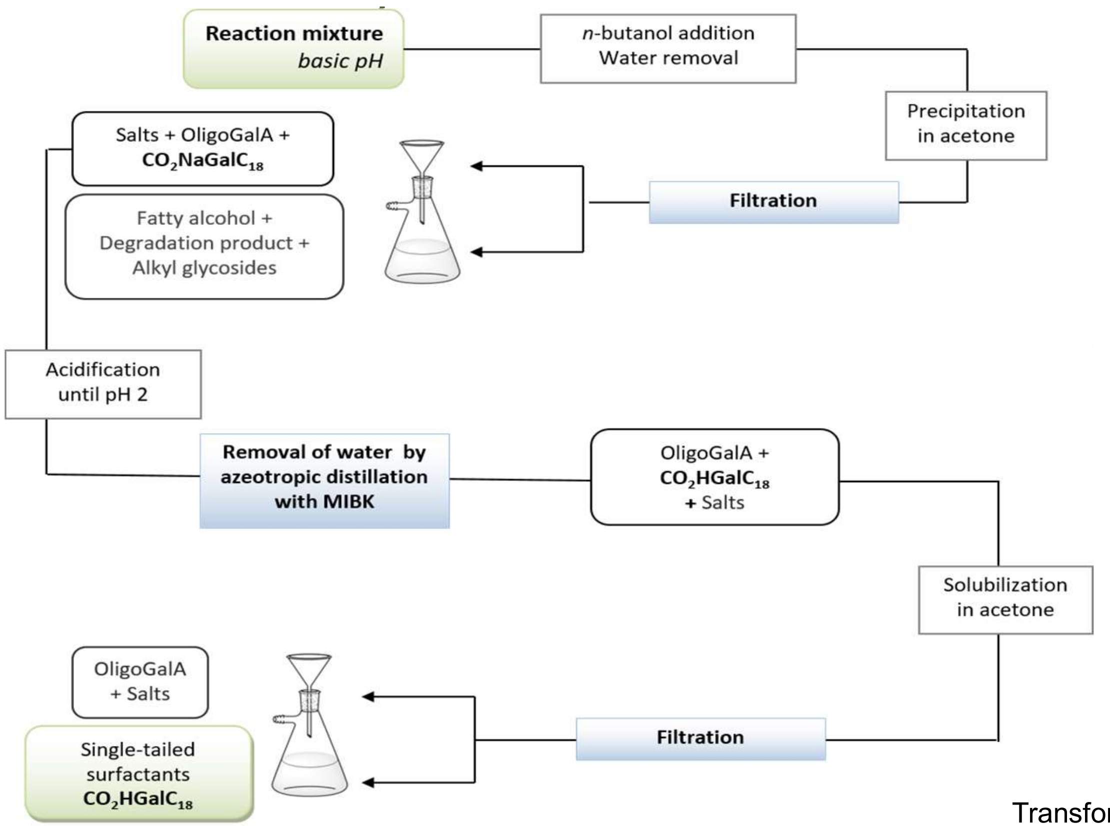
Acidification until pH 2 → **Water removal by azeotropic distillation with MIBK** → **Solubilization in acetone** → **Filtration**

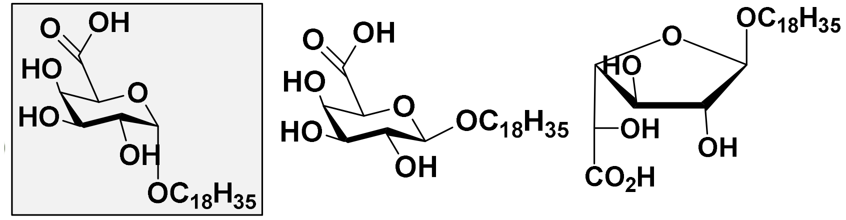


Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, *Molecules*, ***2021***, *26*, 1956.

Anionic Surfactants from Pectins

Hydrolysis / Butanolysis / Transesterification / Transacetalisation / Saponification / Post-reaction Treatment





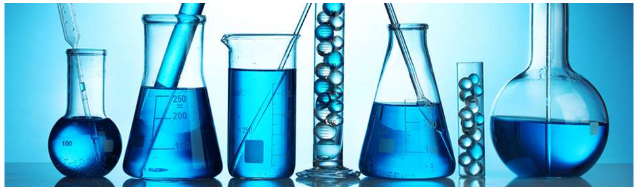
α-D-Gal*p*A β-D-Gal*p*A β-D-Gal*f*A

CO_2HGalC_{18}

- **Overall yield = 62 %; purity > 95% !!**

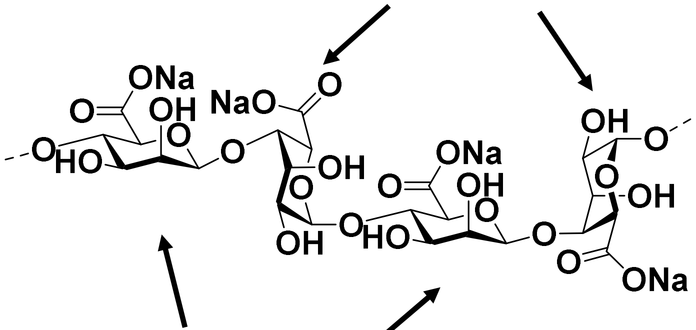
Transformation of pectins into non-ionic or anionic surfactants using a one-pot and cascade mode process, *Molecules*, ***2021***, *26*, 1956.

Anionic Uronate Surfactants from Alginates

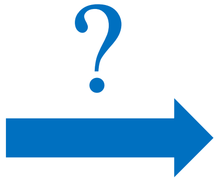


Alginate

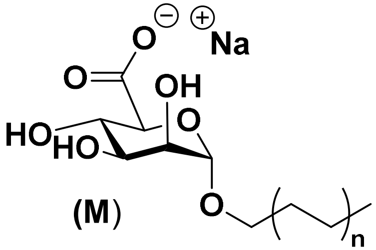
L-Guluronate (G)



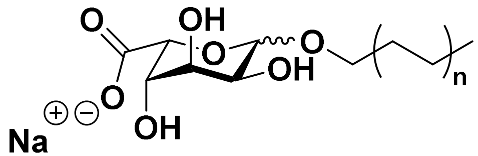
D-Mannuronate (M)



Blue Chemistry



(M)



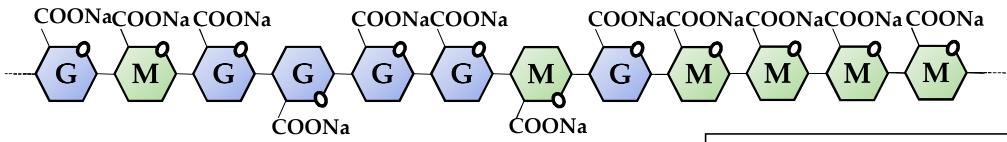
(G)

Anionic D-Mannuronate and L-Guluronate Surfactants

Process for preparing compositions comprising alkyl(alkyl-glucoside)uronates, said compositions and use thereof as a surfactant, ***US*** *2019/0062360 A1*, ***2019***.

Anionic Uronate Surfactants from Alginates

Secondary Structure

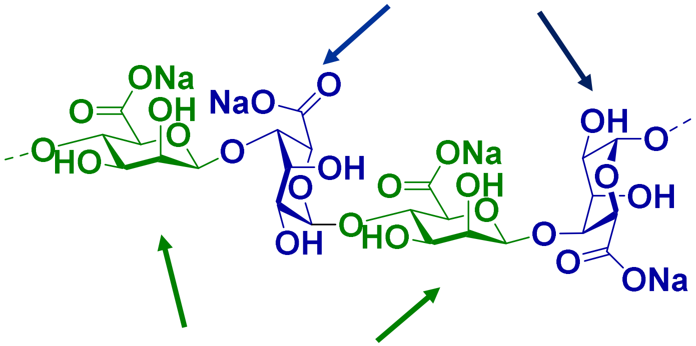


Block copolymers:

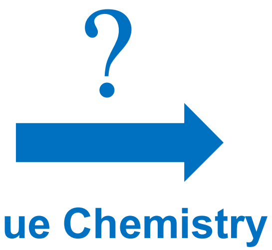
- MM and GG homopolymers
- MG heteropolymers

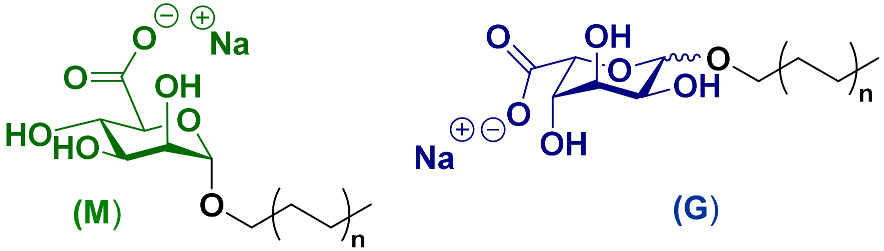
Alginate

L-Guluronate (G)



D-Mannuronate (M)



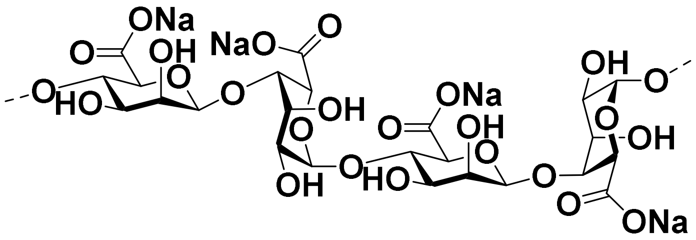


Anionic D-Mannuronate and L-Guluronate Surfactants

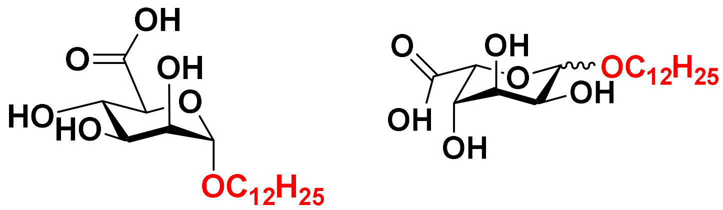
Process for preparing compositions comprising alkyl(alkyl-glucoside)uronates, said compositions and use thereof as a surfactant, ***US** 2019/0062360 A1**, 2019***.

Anionic Uronate Surfactants from Alginates

Alginate



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

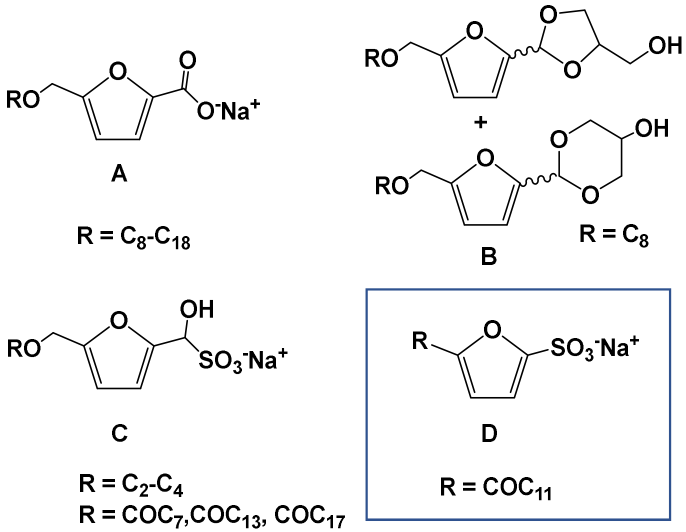


(M) **(G)**

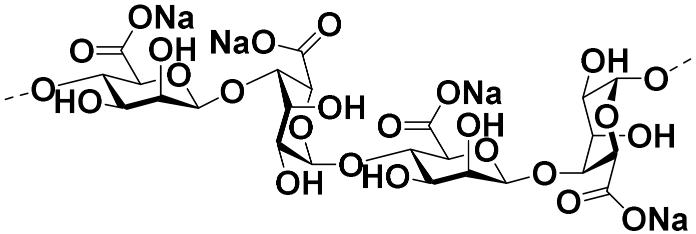
Yield: 45-50%

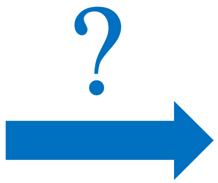
Process for preparing compositions comprising alkyl(alkyl-glucoside)uronates, said compositions and use thereof as a surfactant, ***US** 2019/0062360 A1*, ***2019***.

Anionic Furanic Surfactants from Alginates

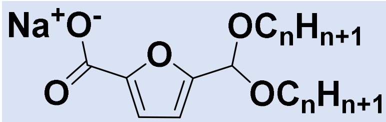


Alginate Oligo- and Polysaccharides





Blue Chemistry



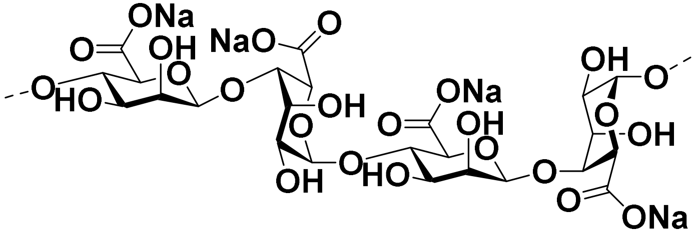
Anionic Furoate Surfactants

Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans, *ACS Cent. Sci*. **2016**, 2, 820.

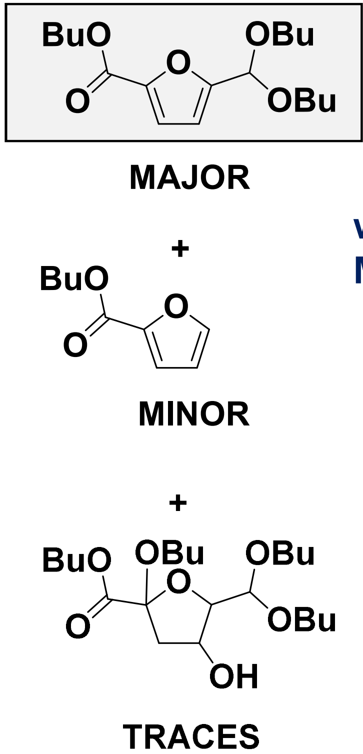
Procédé de synthèse de 5-dialkylacétal-2-furoates d'alkyle et leur utilisation dans la preparation d'agents tensoactifs biosourcés, ***EP** 3560916 A1*, ***2019***.
Direct conversion of alginate oligo- and polysaccharides into biodegradable and non-ecotoxic anionic furanic surfactants – An experimental and mechanistic study, *Adv. Sustain. Syst.,* under revision.

Anionic Furanic Surfactants from Alginates

Alginate Oligo- and Polysaccharides



1) MSA (4.45 - 6 eq.)
H_2O (13 eq.)
n-BuOH (76 eq.)
160°C, 6 h



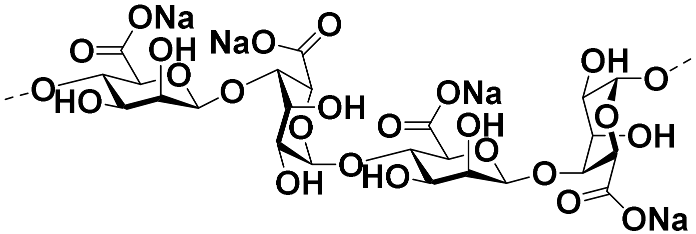
Yield: 30-33%

wt ratio % for
MAJOR/MINOR ≥ 9

Procédé de synthèse de 5-dialkylacétal-2-furoates d'alkyle et leur utilisation dans la preparation d'agents tensoactifs biosourcés, ***EP*** *3560916 A1*, ***2019***.
Direct conversion of alginate oligo- and polysaccharides into biodegradable and non-ecotoxic anionic furanic surfactants – An experimental and mechanistic study, *Adv. Sustain. Syst.*, under revision.

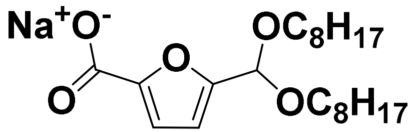
Anionic Furanic Surfactants from Alginates

Alginate Oligo- and Polysaccharides



1) MSA (4.45 - 6 eq.)
H_2O (13 eq.)
***n*-BuOH (76 eq.)**
160°C, 6 h

2) 1N NaOH (2.6 eq.)
Octanol (6.0 eq.)
75°C, 5 mbar, 3.5 h
3) 0.4N NaOH (3.0 eq.)
110°C, 15 h
4) Azeotropic distillation; Filtration of insolubles in water; water removal



$FurCO_2Na$-C_8C_8-based Surfactant composition

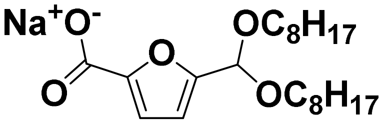
Yield ~ 50%

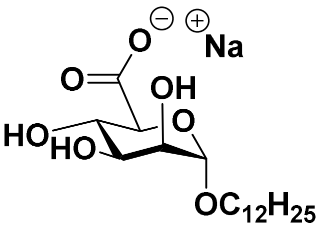
Procédé de synthèse de 5-dialkylacétal-2-furoates d'alkyle et leur utilisation dans la preparation d'agents tensoactifs biosourcés, ***EP** 3560916 A1*, ***2019***.
Direct conversion of alginate oligo- and polysaccharides into biodegradable and non-ecotoxic anionic furanic surfactants – An experimental and mechanistic study, *Adv. Sustain. Syst.*, under revision.

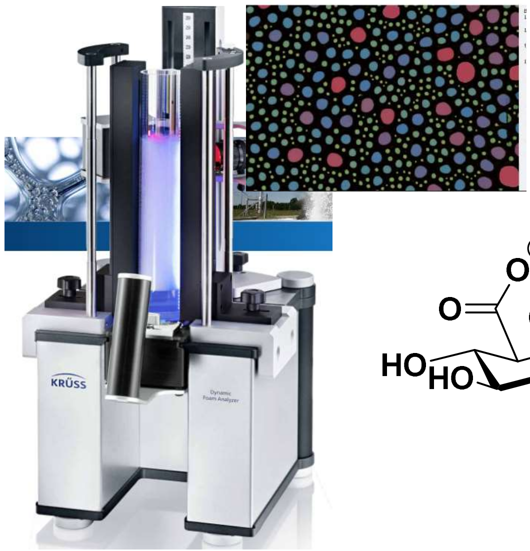
Anionic Surfactants (COONa)

- **Reduction of surface tensions** to values ≤ 32 mN/m at comparable concentrations or at concentrations up to 10 to 15 times lower than the reference petrosourced surfactant (SLES)

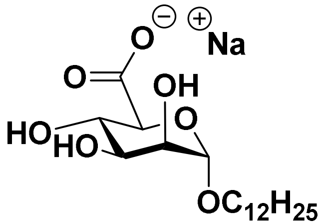
Foaming agent



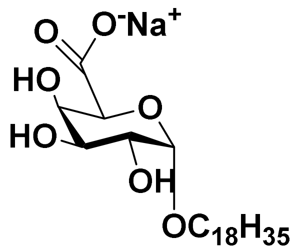




Degreaser



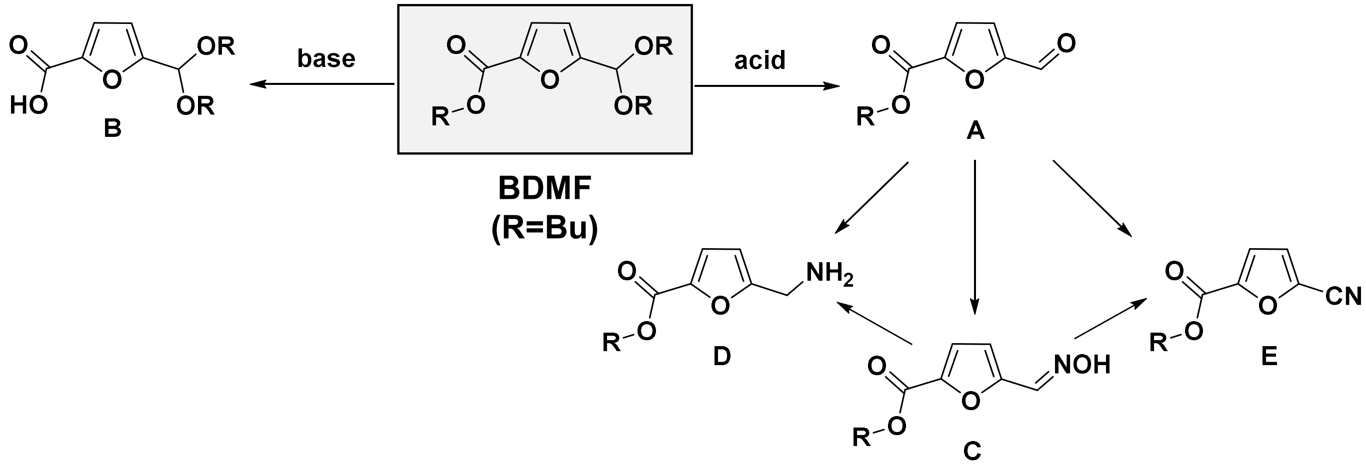
Emulsifier

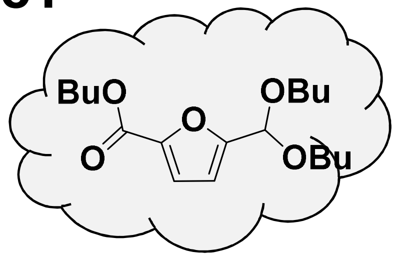


- **Sensory properties** (rich, non-greasy touch): washing/hand and body care solutions

- **Readily Biodegradability** and **absence of any eco-toxicity** (algae, daphnia, fish): OCDE tests

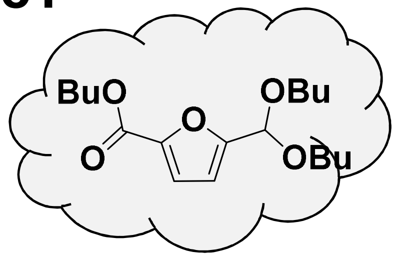
Butyl 5-(dibutoxymethyl)-2-furoate (BDMF): a New Platform Molecule?

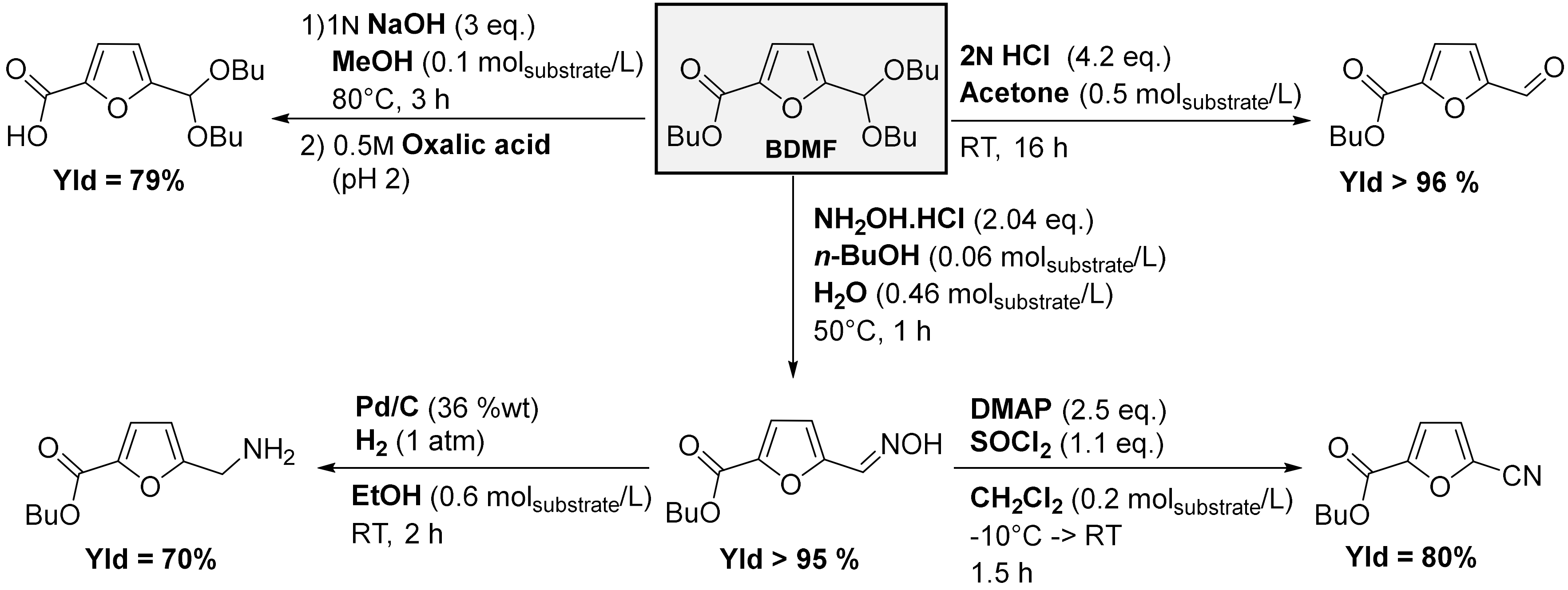




Compound	Domaines d'application	Exemples
A	Pharmaceutique Chimie	(R = PFP) Combinatorial libraries WO02/051775
B	Pharmaceutique Chimie	WO2004037808 (antitumoraux)
C	Polymères Chimie	Intermédiaire de synthèse du caprolactame précurseur du nylon6/nylon12 (production 2 millions de tonnes par an) WO2015060829
D	Polymères Chimie	Précurseur du nylon6/nylon12 WO2015060829
E	Pharmaceutique Polymères Chimie	Inhibiteurs de kinase (anticancéreux) Rhodia (FR2977586, WO2013087765), Bridgestone Corporation (WO2009051700, 2009051702)

Butyl 5-(dibutoxymethyl)-2-furoate (BDMF): a New Platform Molecule?





Acknowledgements

Surfact Green

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ADEME
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UMR CNRS 6226

THANK YOU FOR YOUR ATTENTION