



## PRODUCTION OF TENSIO-ACTIVES FROM OLEAGINOUS PLANTS CHAINS AND POLYSACCHARIDES FROM *ULVA*

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### Introduction

● **PROTOP** (European project) contributes to find a new outlet for *Ulva*, a green algae which produces green tides along European coasts. The aim is to synthesise a new type of biodegradable tensio-active (ulvan ester).

#### Partners of project :

- Javenech S.A. (co-ordinator)
  - ICP (tensio-actives producer)
  - Kavala Oil S.A. (end user)
  - Environmental Protection Engineering S.A. (end user)
  - CEVA
  - ITERG
  - DEMOKRITOS
- } R & D partners

### Structure of ulvans



Picture 1 : Ulvans in natural environment

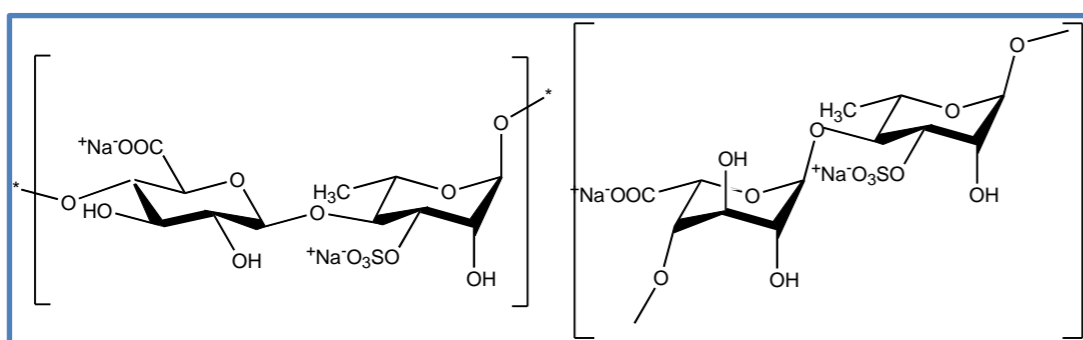


Figure 1 : Chemical structure of two major repeating units in ulvans

### Materials and Methods

#### HPAEC-PAD

- The chemical composition of ulvans is determined by HPAEC-PAD analysis (High Performance Anion Exchange Chromatography - Pulsed Amperometric Detection).
- Sugars are molecules which are electrochemically active. This activity is due to the presence of secondary alcohol functions. The electrochemical detection is based on the capacity of sugars to oxidise themselves at a specific potential (potential between a working electrode and a reference one). The oxidation current produced is directly proportional to the sugar concentration.

#### NMR

- The Nuclear Magnetic Resonance allows to obtain structural knowledge of the compounds for qualitative and also quantitative measure and to control the purity of ulvans samples.

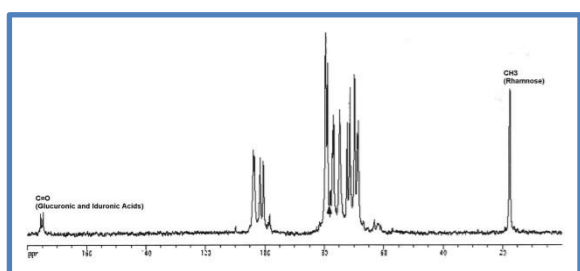


Figure 2 : NMR spectrum of ulvans

Determination of :

- rhamnose content,
- uronic acids (glucuronic and iduronic acids) content.

#### Transesterification Process

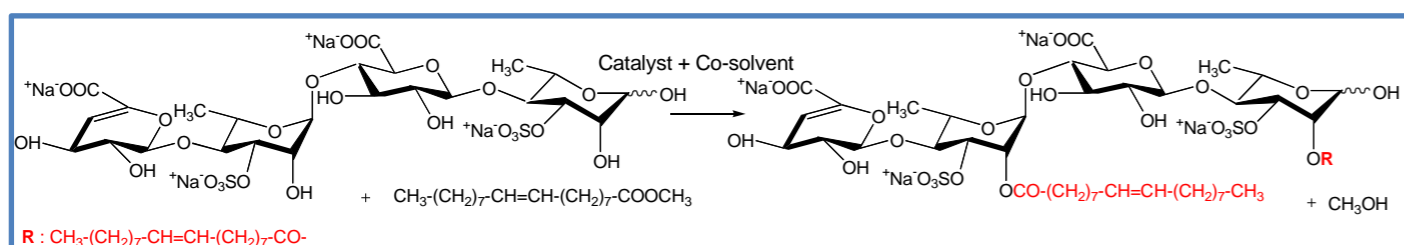


Figure 3 : Transesterification reaction

- The process is performed without solvent which avoids the problems of toxicity and biodegradability.

### Results and Discussion

#### Chemical characterisation of ulvans by HPAEC-PAD

| Sugars         | ITERG Sample      | Ulva Rigida | Ulva Armoricana | Ulva Rotundata |
|----------------|-------------------|-------------|-----------------|----------------|
| Neutral sugars | % Rhamnose        | 1           | 1               | 1              |
|                | % Galactose       | 0.04        | 0.03            | 0.03           |
|                | % Glucose         | 0.12        | 0.11            | 0.22           |
|                | % Xylose          | 0.13        | 0.15            | 0.17           |
| Acid sugars    | % Glucuronic Acid | 0.58        | 0.50            | 0.44           |
|                | % Iduronic Acid   | 0.15        | 0.07            | 0.12           |
|                | % Sulphates       | 0.80        | 0.31            | 0.28           |

Table 1 : Relative ratio of different monomers compared to the principal neutral ose (rhamnose)

- ITERG sample contains numerous sulphates compounds and acids compared to the different species of ulvans, leading to a high polarity of the polysaccharide.

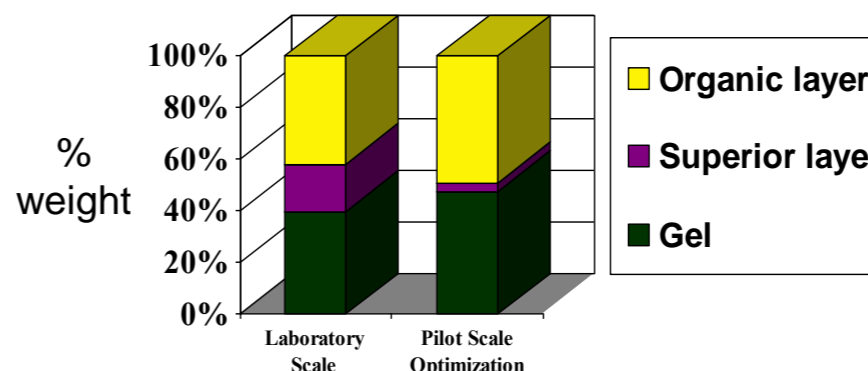
#### Chemical characterisation of ulvans by NMR

% Rhamnose = 60~70%  
% Uronic Acids = 30~40%

#### Transesterification Process

| Synthesis                       | Laboratory Scale | Pilot Scale Optimisation |
|---------------------------------|------------------|--------------------------|
| Grafting ratio of methyl esters | 38.6%            | 20.2%                    |

Table 2 : Characteristics of synthesis



Graph 1 : Proportions of different layers

Three layers are obtained :

- an **organic layer** containing unreacted methyl esters,
- a **superior layer** containing the esterified polysaccharide (EPS),
- a **gel** containing the partially esterified polysaccharide (PEPS).

#### Cosmetic Application

- Industrial valorisation of superior layer and gel

| Analysis                             | Sisterna SP30-C      | Superior Layer (EPS) ITERG Pilot | Sisterna SP70-C        | Gel (PEPS) ITERG Pilot |
|--------------------------------------|----------------------|----------------------------------|------------------------|------------------------|
| Saponification Value (mg KOH/g)      | <138                 | 143                              | Problems of solubility | 77                     |
| Hydroxyl Value (mg KOH/g)            | 326                  | ND                               | 320                    | Not Applicable         |
| Acid Value (mg KOH/g)                | 3                    | 37                               | 3                      | Not Applicable         |
| Hydrophilic Lypophilic Balance (HLB) | 6                    | 13.5                             | 15                     | >20                    |
| Properties                           | Emulsifier Water/Oil | Emulsifier Oil/Water             | Emulsifier Oil/Water   | Hydrophilic Product    |

Table 3 : Comparison between synthesised and commercial products (Sisterna compounds marketed by Unipex)

- **EPS** presents characteristics which are intermediate between Sisterna SP30-C and Sisterna SP70-C. EPS is highly esterified (high saponification value) compared to the gel.

- **PEPS** is partially esterified (low saponification value) and presents high HLB value compared to Sisterna SP70-C.



Picture 2 : gelified product

### Conclusion

This European project opens a new way of industrial development of a biomass (*Ulva* algae) which is considered actually as a waste. The synthesised tensio-actives can be used in different field of application (cosmetic, pharmaceutical, oil spills...).