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Tiana H. Randriamamonjy, Jesus Ontiveros, Mbolatiana Tovo Andrianjafy, Pascal Samiez, Alexandra Berlioz-Barbier, et al.. Comparative study on the amphiphilicity, emulsifying and foaming properties of saponins extracted from Furcraea foetida. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 653, pp.129923. 10.1016/j.colsurfa.2022.129923 . hal-04094860

HAL Id: hal-04094860
https://hal.univ-lille.fr/hal-04094860v1

Submitted on 1 Dec 2023

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Comparative study on the amphiphilicity, emulsifying and foaming properties of saponins extracted from *Furcraea foetida*

Tiana H. Randriamamonjy[1], Jesús F. Ontiveros[2*], Mbolatiana Tovo Andrianjafy[1], Pascal Samiez[3], Alexandra Berlioz-Barbier[3], Véronique Nardello-Rataj[2], Jean-Marie Aubry[2], Voahangy Ramanandraibe[1*], Marc Lemaire[1,3]

[1]*International Associated Laboratory, University of Antananarivo-Lyon 1, PO Box 906, Antananarivo, Madagascar*
[2]*Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181– UCCS –Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.*
[3]*ICBMS, UMR 5246 CNRS UCBL1rue Victor Grignard 69100 Villeurbanne*

jesus-fermin.ontiveros@centralelille.fr, voahangy.vestalys@yahoo.fr

Abstract

A sustainable surfactant was obtained as a by-product of waste from the production of fibers from *Furcraea foetida* (FF). The extraction process is described and the chemical constituents (flavonoids, saponins and others) in the hemp of Mauritius in Madagascar were determined using ultra-performance liquid chromatography coupled to high resolution hybrid mass spectrometer. The hypothesis of surface-active behavior of this crude mixture was corroborated by surface tension measurements and these results were compared with 2 commercial *Quillaja saponaria* (QS) samples: S0019 (TCI) and Q-Naturale 200V. The critical micellar concentration of the FF saponins is 0.025 wt.%. The hydrophilicity-lipophilicity radius was determined by the PIT-slope method and all saponins are more hydrophilic than the $C_{10}E_4$, the polyethoxylated reference surfactant. The hydrophilicity decreasing order is as follows: Q-Naturale 200V > *FF* > S0019. Oil in water (O/W) emulsions were formulated with isopropyl myristate as oil and their size distribution and stability during 7 days are equivalents for the three saponins. There is no coalescence, and creaming phenomena can be reduced increasing the oil fraction. Nanoemulsions were obtained with FF using ultrasounds and reducing the oil content. Foaming properties were also studied and the stability of foams is similar between the 3 saponins (higher than the foam formulated with sodium laureth sulfate). These findings show that FF is a new source of saponins that can be used as promising emulsifier and foam agent with properties equivalent to those quantified for available commercial saponins and equal or better than typical benchmark surfactants as Tween 40 (emulsifier) or sodium laureth sulfate (foaming agent).

Keywords: *Furcraea foetida, saponins, PIT-slope, emulsion, foam.*

1. Introduction

Mauritius hemp or *Furcraea foetida* (Asparagaceae) called "*taretra vavy*" in Madagascar, is a plant native of tropical America and found often in dry and warm areas [1]. Generally, people use this plant as a source of fiber but in some isolated localities of the island, leaves containing saponins [2–4] serve as soap. The species is a non-wood plant used to make paper [5] or in composite manufacture. Totong et al. [6] reported that from 2,5 kg of *Furcraea foetida* leaves, only 25 grams (1%) of fiber could be removed. Subsequently, the production of natural fibers from *Furcraea foetida* generates a large amount

(64% wet mass [7]) of wood waste known as "chenevots" which consist of small fibers and a wide variety of chemicals, including sugar and secondary metabolites such as saponins and flavonoids among many others [8]. The renewed interest in natural fibers as alternatives to non-biodegradable or synthetic fibers induces an increase in production and requires the search for processes limiting the production of waste.

Saponins are vegetal glycosides with an aglycone moiety and one or up to 3 sugar chains (hexoses like ß-D-glucose, or pentoses like ß-D-arabinose). The aglycone moiety is the sapogenin and its structure can be a steroid or a triterpenoid [9]. In most cases, saponins serve as an anti-microbial defense in plants, they have a hemolytic action, steroid-complexing properties and surfactant activity [9,10]. The surfactant activity of saponins is well documented and as early as 1869, a USA patent indicates the "cleansing" properties of the fluid obtained from the bulb of *Phalangium pomeridianum* chemically treated with borax and salt-soda [11]. The emulsifier properties of saponins were already mentioned in 1903 by Hillyer [12], and also by Ramsden in 1904 [13] and Pickering in 1907 [14]. However, the early interest on their surfactant properties declined by the exponential development of synthetic surfactants as detergents, emulsifiers, wetting or foaming agents that takes place in most of the XX century [15].

Since the end of the XX century and until our days, there is increasing interest in replacing petro-sourced synthetic surfactants with bio-sourced compounds in most of the formulation fields. This trend is the result of both industry efforts and consumer awareness about the environment. The commercial preparation of saponin from *Quillaja saponaria* is generally recognized as safe (GRAS) in the USA [16]. The European Union authorizes the "Quillaia extract" in food formulations (additive E-999), specially beverages; their authorities regulate its concentration at 200 mg/Kg and the origin of the saponins is clearly established as the product of "extraction of *Quillaia saponaria Molina*, or other *Quillaia* species, trees of the family *Rosaceae"* [17]. The Food and Agriculture Organization classifies the Quillaja extracts in Type 1 or 2 depending on the composition; type 1 contains over 100 triterpenoid saponins with polyphenols and tannins and type 2 is obtained after ultrafiltration of type 1, reducing the solids and polyphenols [18].

Since the incorporation of saponins in food, cosmetic and pharmaceutical formulations, the industrial and academic interest in these molecules has increased in order to expand their uses to other fields like enhance oil recovery [19], soil remediation[20], micellar enhanced ultrafiltration [21], adjuvants [22], encapsulation [23] or nanoparticles synthesis [24]. Several works have been made to understand their interfacial properties [25–28] and their behavior in complex food matrices [29], and also to describe the chemical composition and applications of saponins from vegetal sources different to the well-known *Quillaja saponaria* [30–34].

The main objective of this work is to study the extraction of saponins from chenevots of *Furcraea foetida*, to describe their chemical structure and to characterize some physicochemical properties of the saponins extract. The surface tension, the hydrophilic-lipophilic ratio quantified by the PIT-slope method, and the emulsifier and foaming properties are analyzed and compared with available commercial saponins. These properties allow evaluating the surface potential applications for these saponins that could be easily obtained from the chenevots (wastes) in Madagascar.

2. Material and Methods

2.1 Materials

Quillaja saponin (Q-Naturale 200V) was kindly provided by Ingredion Germany GmbH (Hamburg). This product is a brown liquid containing 14.5wt% of saponins from Quillaja *saponaria Molina.* Saponin

S0019 is a brown powder obtained from TCI (Japan). Tetraethyleneglycol monodecyl ether $C_{10}E_4$ (>99%) was synthetized and distilled in the laboratory following a method described elsewhere [35]. n-Octane (99%) and isopropyl myristate (>98%) were obtained from Sigma-Aldrich. Sodium chloride NaCl (≥99.5%) was supplied by Acros Organics. Texapon N70 (alcohols, C_{12-14}, ethoxylated sulfates sodium salts 1-2.5EO at 70%) and Polysorbate 40 were obtained from BASF and AlfaAesar, respectively.

2.2 Extraction of saponins from *Furcraea foetida*

The raw material was dry chenevots from *Furcraea foetida*. They were collected in the village of Anjanonarivo, located 40 km northwest of the city of Antananarivo, Madagascar. They are obtained from fresh scraped leaves to separate fibers from chenevots. These chenevots were air-dried for 2 days.

200 g of dry chenevots were extracted on Soxhlet with 1250 mL of n-butanol for 6 hours. The solution was evaporated to dryness (R = 12.2%) and precipitated in ethyl acetate to remove the non-polar fraction (soluble fraction, R = 5.8%). After washing and filtration, the insoluble extract was recrystallized in isopropanol to give saponins with 2.1 % yields from dry weight. Flavonoids and other compounds were soluble in isopropanol. Extraction process is schematized in figure 1.

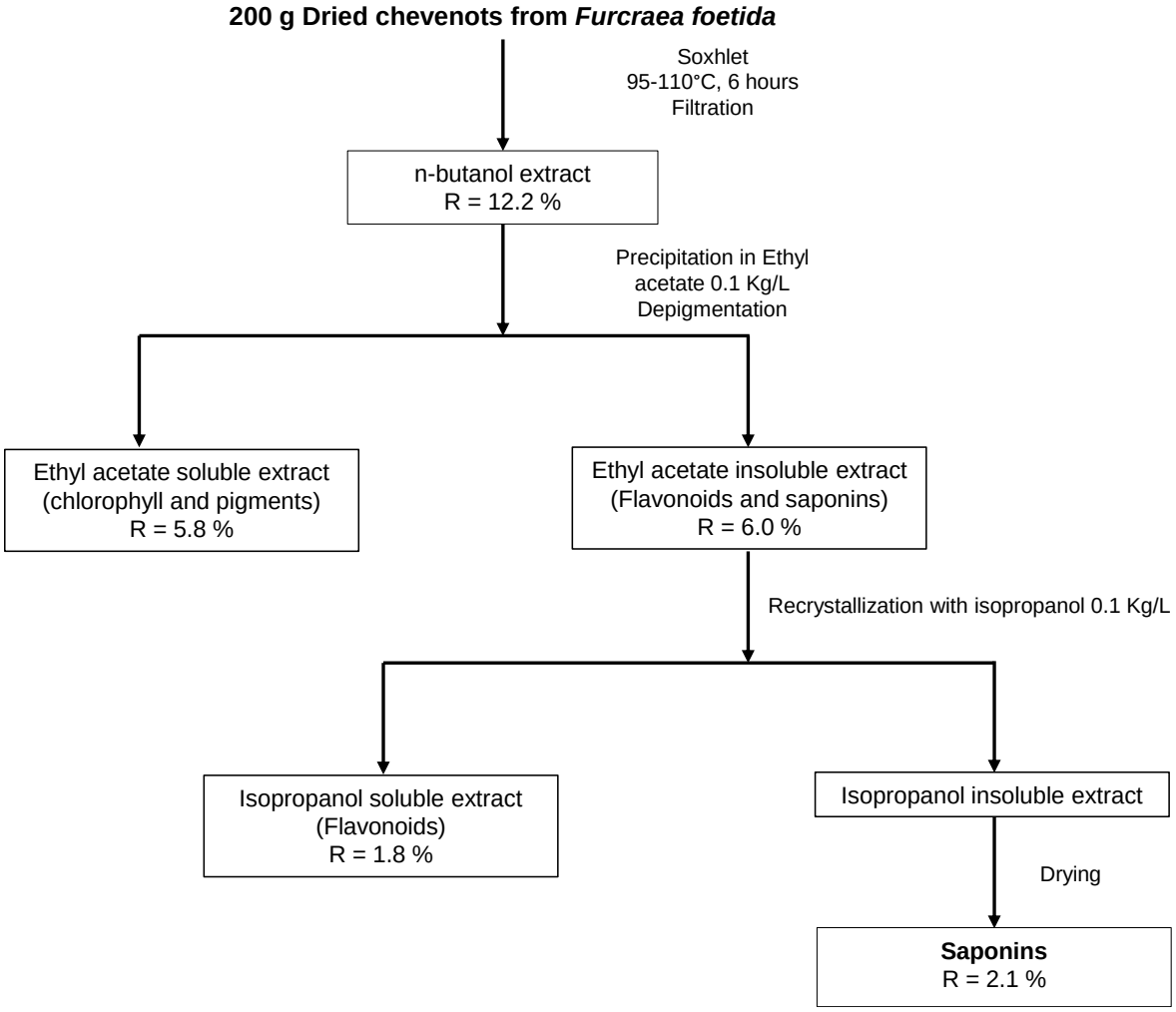


Figure 1. Extraction procedure of saponins from *Furcraea foetida.*

2.3 Analysis by UPLC-ESI-HRMS:

Equipment. Structural identification was performed in high pressure liquid chromatography coupled with mass spectrometry (LC/MS) at the Institut de Chimie, de Biochimie Moléculaire et Supramoléculaire (ICBMS), University of Claude Bernard Lyon 1 using ultra-performance liquid chromatography (UPLC-U3000, Thermo Fisher Scientific) coupled to a high resolution hybrid mass spectrometer of four pole time flight type.

Sample preparation. 25 mg of saponins were mixed in 2 mL of methanol and acetonitrile by using a vortex. The solution was immersed in an ultrasonic bath for 5 min and diluted in 2.5 ml of water before being centrifuged at 10000 rpm for 10 min until the saponins are completely dissolved.

Chromatographic conditions. The saponin extract was analyzed on a C18 column CSH dimension 2,1 mm x 150 mm, particle size 1.7 µm (Waters), maintained at 45 °C. The mobile phase consisted of water (A) and Acetonitrile/Methanol (B), each containing 0,1 % (v/v) formic acid with the gradient of 100% of phase A for 2 min, followed by a linear increase of 0 to 100% phase B for 38 min. The flow rate was established at 400 µL/min and the injection volume was 50 µL.

Mass spectrometry detection. The ESI-MS spectra were acquired in positive and negative ion modes. The ionization source was maintained at 200°C with a constant pressure of 45 Psi. The Acquisition mode Auto MS / MS (DDA) was used and its frequency depends on the intensity. Mass range was about 150-3000 Da. XCMS software was performed for data analysis.

2.4 Surface tension measurement.

A force tensiometer “K100" with a Wilhelmy plate was used to measure the surface tension of several aqueous solutions of saponins at 25°C (±0.5°C). Highly concentrated stock solutions above the expected critical micelle concentration were serially diluted to at least 0.001 wt% saponin.

2.5 PIT-slope method.

Either the sample preparation, the heating-cooling cycles and the phase inversion temperature determination were done under the conditions previously described in the literature [36,37]. The analyzed surfactants were added to the reference system 3% wt. $C_{10}E_4$/*n*-octane/0.01M $NaCl_{(aq)}$ with a weight ratio water/oil of 1 (f_w=0.5). The phase inversion temperature (PIT) at different concentrations of the studied surfactant “S_2” was determined by the fall of the conductivity with temperature. All saponin samples were studied in a range of concentrations until 1 wt.%. The weight concentration of saponin is defined in these experiments as:

$$\%\text{wt.} = \frac{m_{Saponin}}{m_{C_{10}E_4} + m_{Saponin} + m_{octane} + m_{water}} \quad (1)$$

2.6 Emulsion preparation and characterization protocol

Saponine/Isopropyl myristate/0.01M NaCl(aq) system were prepared 24h before the experiments at different concentrations of saponin and different mass fractions of water. In the case of 1%wt Saponin and f_w=0.5, samples were prepared by pouring 4.25g of water, 4.25g of isopropyl myristate and 0.086g of saponin (or the equivalent when the saponin is in aqueous solution as in the Q-Naturale case); then the samples are gently mixed to put in contact the different phases. Samples are homogenized with IKA Ultraturrax T-10 basic with a S10N-8G dispersing tool (8mm stator diameter and 6.1mm rotor diameter) during 60 s at 16000 rpm or sonicated for 2 min using an ultrasonic probe Sonotrode S26d2 (2 mm diameter) immersed by 3 mm in the system and operated by the ultrasonic processor UP200St (Hielscher). The sonotrode pulse was fixed at 100% and the amplitude at 80%. The emulsion droplet size distribution was determined using a laser diffraction instrument (MasterSizer3000, Malvern Instruments). The emulsion stability was measured at constant temperature (25°C) by multiple light scattering using a Turbiscan Lab Expert (Formulaction).

2.7 Foaming and foam stability

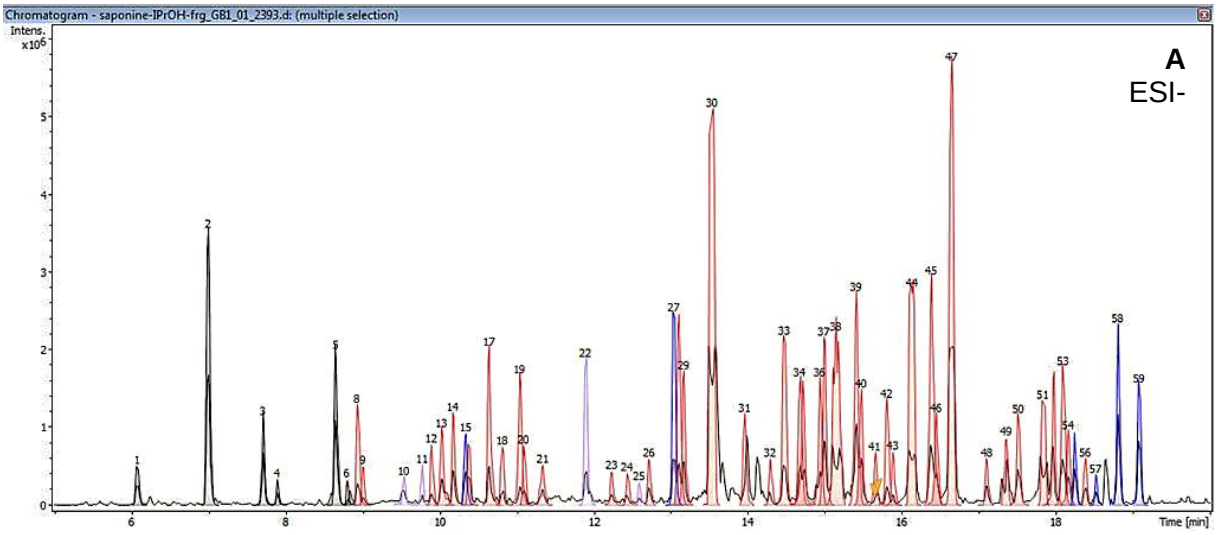
The foaming properties of the saponins were studied using the DFA-100 from Krüss (Hambourg, Germany). The concentration was fixed at 2 times the CMC for all samples. 50 mL of the solution were added to the glass column CY4572. Pressurized air was sent to the column through a filter paper FL4551 (12-25 µm) at a rate of 0.2 L/min and foaming was stopped at a total height (liquid+foam) of 180 mm. The foam (h_{foam}), liquid (h_{liquid}) and total height (h) were monitored for 20 min after the 180mm were reached. Bubbles size distribution was monitored by the ADVANCE software at a height of 10 cm. All experiments were done at least by triplicate. The maximum foam density (FD) and the foam stability (FS) at 1200 s are defined as follows:

$$FD_{t=0} = \frac{V_{liquid\ in\ the\ foam}}{V_{foam}} \times 100 \qquad (2) \qquad FS_{t=1200} = \frac{h_{foam\ t}}{h_{foam\ t=0s}} \times 100 \qquad (3)$$

3 Results and Discussion

3.1 Structural analysis

UPLC coupled with mass spectrometry was carried out to distinguish saponins in final sample. Raw formulas of different molecules were identified by comparing mass spectra with databases such as PubChem, ChemSpider and the MS/MS fragments with MetFrag database. Figure 2 shows the chromatographic profile of the isopropanol insoluble extract. Peak numbers correspond to ascending order of molecules retention times and polarity. The most polar compounds were first eluted and had low retention times. Functional groups and double bonds on genins are responsible for their polarity followed by number and nature of sugars in glycosidic moieties.



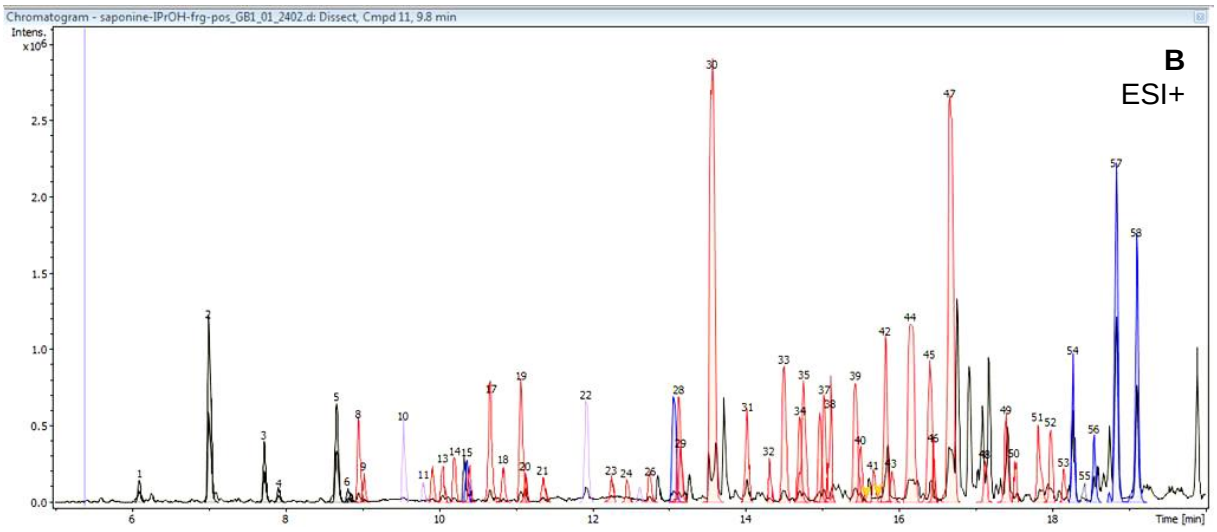
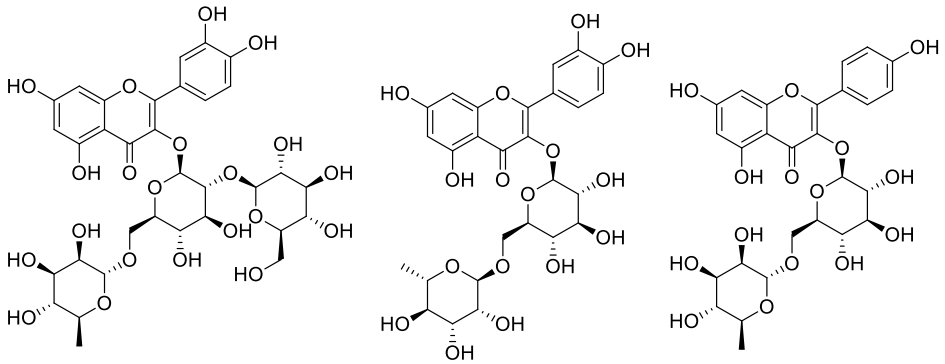


Figure 2. Chromatographic profiles (LC/MS) of insoluble isopropanol extract from *Furcraea foetida* leaves. A) Chromatogram in negative mode (ESI-). B) Chromatogram in positive mode (ESI+).

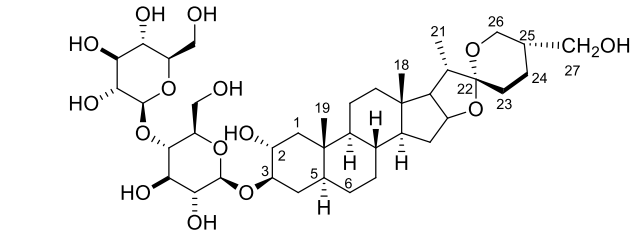
The chromatograms A and B exhibit peaks grouped into different colors according to their chemical family such as saponins (red), flavonoids (black) and other compounds (blue, purple, orange). According to the LC/MS analysis, isopropanol insoluble products consist mainly of saponins and some flavonoids. Vanitha *et al.* [8] have revealed that other groups of compounds like carbohydrates and tannins (peaks with other colors) have also been found in the plant. Most of saponins and flavonoids have been previously isolated from leaves of *Furcraea foetida* [4] or found in others *Furcraea* species [3,38–40].

All the saponins identified are of the steroid type (spirostanol and furostanol ones). Two large peaks were listed and corresponded to a crestagenin 3-*O*-*β*-D-glucopyranosyl-(1→4)-*O*-*β*-D-glucopyranoside (peak N°30) and a chlorogenin 6-*O*-[*β*-D-glucopyranosyl]-(1→4)-*O*-*β*-D-glucopyranoside (peak N°47). We note that peak N°30 has the same molecular formula $C_{39}H_{64}O_{15}$ than cantalasaponin-1 identified previously in *foetida*, *hexapetala* and *tuberosa* species of the genus *Furcraea* but according to its retention time and polarity, we assigned the sapogenin to the crestagenin [41], a diastereosiomer of chrysogenin, with the same sugar unities. This compound was already found in *F. tuberosa* and had a *25-R* configuration with three hydroxyl groups (27,*2α*,*3β*) instead of *23S*,*3β*,6*α* like in chrysogenin.

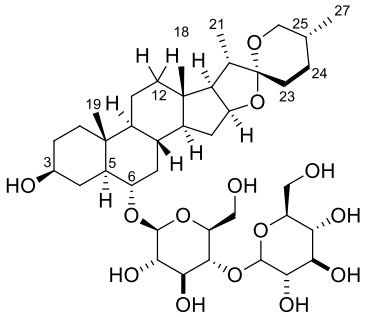
Some flavonoids peaks have higher retention times than saponins because of the hydroxyl groups in the aglycon skeletons inducing their polar structures. By comparing the mass spectra of each peak with those of compounds previously isolated from *Furcraea* genus, we have identified Kaempferol or Quercetine derivatives for the major peaks such as Camelliaside A (peak N°2), Rutin (peak N°4) [40] and Nicotiflorin (Peak N°5) [40]. In our knowledge, Camelliaside A is described for the first time in *F. foetida*. Camelliaside B was found in *F. tuberosa*. Figure 3 shows some of the chemical structures of different compounds found in the FF.



Camelliaside A (2) **Rutin (4)** **Nicotiflorin (5)**



Crestagenin 3-O-ß-D-glucopyranosyl-(1➔4)-O-ß-D-glucopyranoside (30)



Chlorogenin 6-O-[ß-D-glucopyranosyl]-(1➔4)-O-ß-D-glucopyranoside (47)

Figure 3. Structures of flavonoids and two major saponins in *Furcraea foetida*

3.2 Amphiphilic properties

3.2.1 Self-aggregation behavior

Figure 4 shows the surface tension profiles at 25°C as a function of the saponin weight concentrations between 0.0001 wt.% and 1 wt. %, not only for the *Furcraea foetida* but also for two saponins commercially available.

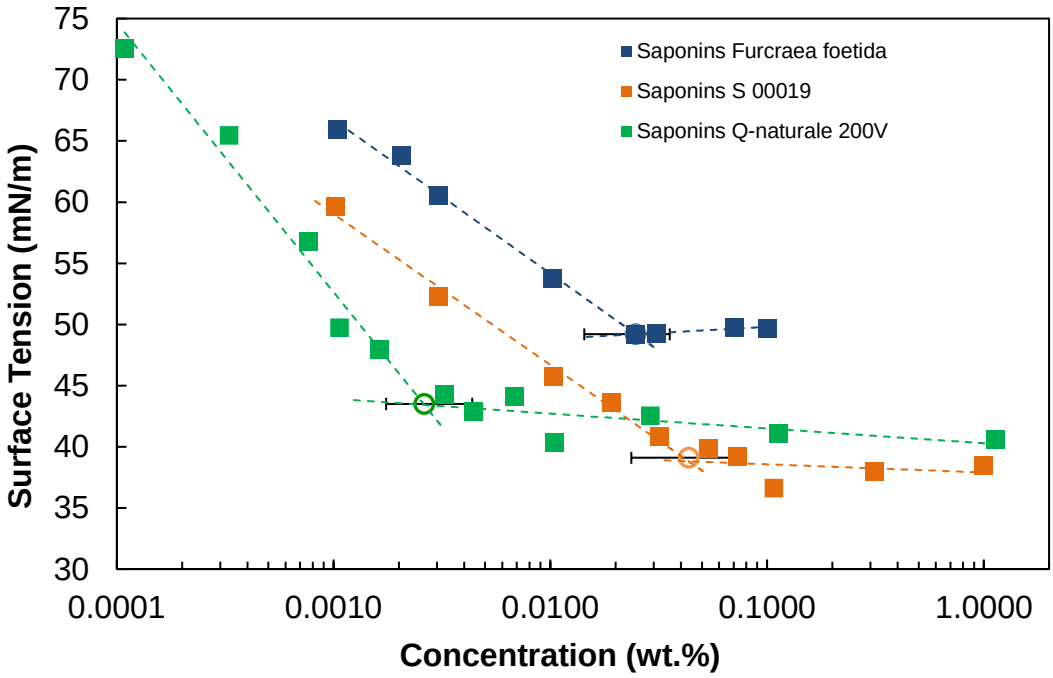


Figure 4. Surface tension profiles as a function of saponin concentrations (wt.%). Dotted lines indicate the logarithmic fit. Empty cercles indicate the CMC. Confidence limits of CMC are calculated as recommended by Miller [42].

The CMC and the surface tension at CMC (γ_{CMC}) were determined from the breakpoint of the surface tension *versus* surfactant concentration profiles. The values of maximum surface excess (Γ) and the area per molecule at the interface (a_1^s) were also calculated using the Gibbs isotherm equation, expressed as follows for a nonionic surfactant:

$$\Gamma = -\frac{1}{2.303RT}\left(\frac{d\gamma}{dlogC}\right)_T \quad (4)$$

where γ is the surface tension (mN/m), T is the absolute temperature (K), R= 8.314 J/mol·K. The area per molecule at the interface (a_1^s) is expressed in square angstroms using eq. 5:

$$a_1^s = \frac{10^{16}}{N\Gamma} \quad (5)$$

where N is the Avogadro's constant and Γ is expressed in mol/cm^{-2}. Table 1 shows the CMC, the surface tension at the CMC, the maximum surface excess and the area per molecule at the water-air interface.

Table 1. Critical Micellar Concentration (CMC), surface tension at CMC (mN/m), surface excess concentration of saponins (mol/cm^2), area per molecule ($Å^2$), PIT-slope (°C/wt.%)

Surfactants	**CMC (wt.%)**	**γ_{CMC} (mN/m)**	**$\Gamma_{max}\cdot10^{10}$ (mol/cm^2)*[a]**	**a_1^s ($Å^2$)**	**PIT-slope (°C/wt.%)**
Saponins from *Furcraea foetida* (FF)	0.024	49.2	2.2±0.1	75±4	10.2±0.8
Saponin S 0019 (TCI)	0.043	39.1	2.2±0.1	77±4	9.5±0.2
Q-Naturale 200V (Ingredion)	0.0026	43.5	3.9±0.4	43±5	18±1

[a] Note that the surface excess can be calculate without knowing the molecular weight of the sample because the units of the concentration on equation 4 are irrelevant $dlogC \cong \Delta\log C = \log(C_1/C_2)$.

The CMC of *Furcraea foetida* saponins is on the order of magnitude of *Quillaja saponaria* and its value is between that of Q-Naturale 200V and that of TCI. The CMC of saponins depends notably on their botanical origin and values from 0.008 (*Aesculus hippocastanum*) to 0.3 wt% (*Acacia concinna*) are reported in the literature [25]. Previous studies for *Quillaja saponaria* saponins shows also CMC values from 0.05-0.08%wt./v [43], 0.025%wt. [44], 0.017%wt./v [45], 0.005%wt. [46] and 0.008%wt. [28]. The differences in these values indicate that not only the origin but also the purification steps in the extraction process change the chemical composition and the surface properties of saponins. The surface tension at the CMC for the two commercial saponins are similar to those reported by Stanimirova *et al.* [44] (38-40mN/m). The value for FF is higher than others, indicating a lower surface activity in aqueous solution. The area per molecule is an average value of different molecules present in the samples and the obtained value for FF extract is close to the reported for other saponins as *Gypsophila* (triterpenoid aglycone) or *Tribulus terrestris* (steroid aglycone) which are 77 and 66$\dot{A}^2$, respectively. Molecular modeling have been reported [44] and several configurations at the interface are proposed for triterpenoid aglycone depending on the "average" value of a_1^s [27]. However, there is no available molecular modeling data about steroidal saponins present in FF extract to conclude about their spatial configuration.

3.2.2 Amphiphilic behavior in Surfactant/Oil/Water systems

The PIT-slope method allows evaluating the hydrophilic-lipophilic behavior of a surfactant thought a temperature dynamic scan. Aliquots of the studied surfactant are added into a reference system 3 % wt. $C_{10}E_4$/*n*-octane/10^{-2}M $NaCl_{(aq)}$ and the linear variation on the phase inversion temperatures allows calculate the dPIT/dC or "PIT-slope", a comparative criterion that indicates if the surfactant is more or less hydrophilic than $C_{10}E_4$. Figure 5A shows the conductivity profile of the reference system when adding saponins from *Furcraea foetida.*

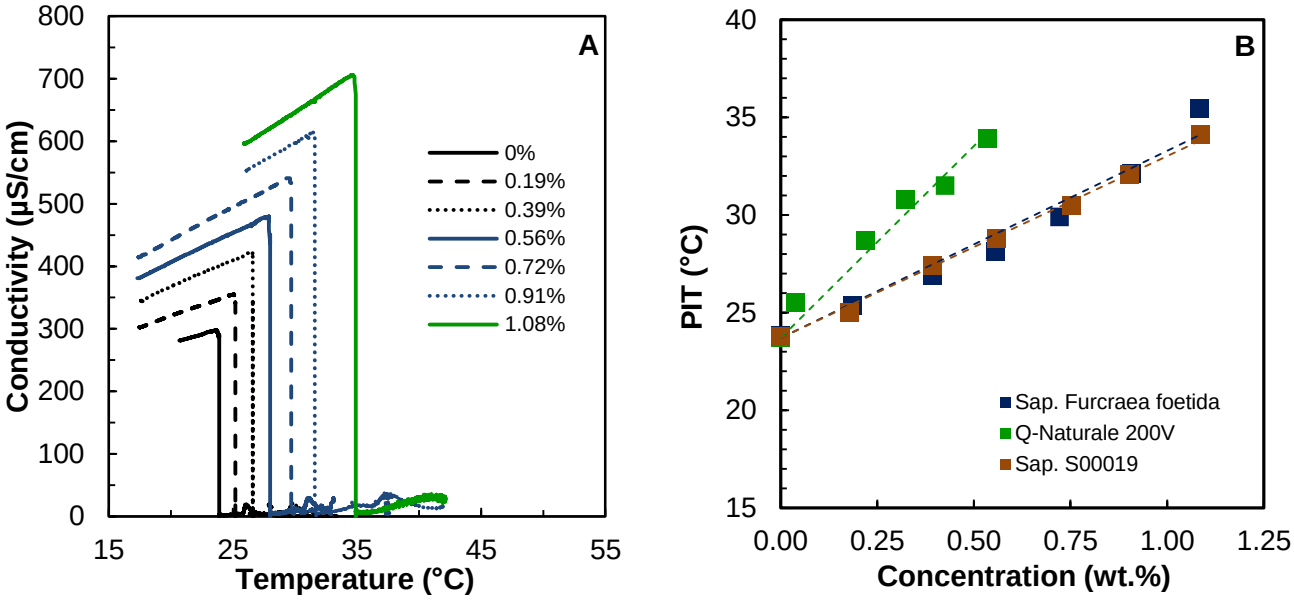


Figure 5. A) Conductivity-Temperature profile at several weight percentages of saponins from *Furcraea foetida*. (Data from the second heating cycle). B) Phase inversion temperature of the system 3 wt.% $C_{10}E_4$/n-octane/0.01M $NaCl_{(aq)}$ at f_w=0.5 versus weight percentage of added saponins. Data from the second heating cycle.

Increasing temperature induces a phase inversion from O/W to W/O by the dehydration of polyethoxylated groups of $C_{10}E_4$. When the concentration of saponins increases, the PIT also increases. Furthermore, if the conductivity profiles in the O/W zone are compared at a constant temperature it is clear that the addition of saponins increase the conductivity of the aqueous phase. This result suggests

that ionic compounds (salts/acids) are present inside the saponin extract. This behavior is obtained for all studied saponins and it is more pronounced for the Saponine S 0019 and Q-Naturale 200V (see Supplementary Information).

Figure 5B shows the evolution of the PIT at several concentrations of saponins. In all cases, a higher temperature than the reference $C_{10}E_4$ is needed to inverse the emulsion indicating that added saponins are more hydrophilic than $C_{10}E_4$. From the figure 5B, the PIT-slope can be calculated for all saponins as shown in table 1 and classified in decreasing order of hydrophilicity: Q-Naturale 200V > *Furcraea foetida* > S0019 (TCI). Using these values, their PIT-slope can be compared with other technical-grade or well-defined surfactants published in the literature [36,37].

The value of dPIT/dC = 10.2°C /%wt. for *Furcraea foetida* saponin matches with the value of Tween 40 which is a commercial polyethoxylated sorbitan monopalmitate surfactant used as an additive in the food industry (E-434). The PIT-slope of saponins are comprised in the $C_{12}E_6$-$C_{12}E_{10}$ hydrophilicity interval.

From 0.54% by mass for saponin Q-Naturale 200V, the emulsion does not inverse in the temperature range studied, indicating a highly hydrophilicity compared with the other saponins. No matter the temperature this system remains as an O/W emulsion at this concentration as reported previously for well-defined ionic surfactants at lower concentrations [37]. The presence of acid groups in some saponins has been established by FTIR, their influence studied in several works [28,47] and the question about the non-ionic or ionic behavior of saponins is still open. Böttchet and Drush [28] determined the CMC of 6 saponins with a conductivity titration, common for ionic surfactants, and the characteristic break was observed for 4 saponins (*Quillaja saponaria* Molina, *Gypsophila*, *Aescumus hippocastanum* and *Glycyrriza glabra*) that were considered as "ionic compounds". The "acidity" of Q-Naturale 200V and the influence of pH on its interfacial behavior at air-liquid interface have been described by Ulaganathan *et al.*[47]. The conductivity and pH of FF saponins were evaluated as a function of the concentration (see Figure SI.1 in the supplementary information). Increasing the concentration of FF saponins diminishes the pH and increases the conductivity. A solution 1 wt% has a pH of 5.1 and a conductivity of 0.65mS/cm, verifying the presence of ionic compounds and their slightly acid character.

3.3 Saponins in dispersed systems

3.3.1 Emulsifier properties

The ability of the three saponins to stabilize emulsions of water and isopropyl myristate (IPM) (50/50 w/w) was then investigated. Equal weight fractions of aqueous and oily phase were chosen in order to privilege the nature of the surfactant on the final morphology of the emulsion. All systems were oil-in-water emulsions (O/W), in agreement with the hydrophilic nature of saponins as quantified by the PIT-slope method. Indeed, Q-Naturale 200V and Tween 80 emulsions have been compared by Yang *et al.* [48] in the formulation of O/W food emulsions, showing that they have similar interfacial properties. Figure 6A indicates the influence of 1wt.% saponin surfactant on the droplet distribution of model emulsion formulated under the same stirring conditions (2min at 16000rpm Ultraturrax).

At first sight, all systems present a monomodal distribution. However a small population (indicated by the corresponding color arrow in **Figure 6A**) is always present with droplet diameters smaller than those of the major distribution, explaining the lower calculated values of the Sauter mean diameters ($d_{(3,2)}$) compared with the apparent mean volume diameter ($dv_{0.5}$). FF saponin shows a slightly lower $d_{(3,2)}$ than the two commercial saponins (17.1 μm *versus* 23.9 and 24.4 μm). Figure 6B and 6C shows the photo of emulsions formulated with Q-Naturale 200 and FF observed by optical microscopy confirming the distribution size obtained using the Mastersizer 3000. Although the droplet size is relatively large, no coalescence was observed in any of the samples during the 7-days period. However, all samples presented, as expected, a slow creaming phenomenon as indicated by the transmittance profiles from

Turbiscan (see the FF profile on Figure SI3 in the supplementary information). The absence of coalescence confirms the good emulsifying properties of saponins as reported in the literature [16]. All these findings show that FF saponins also have very good emulsifying properties.

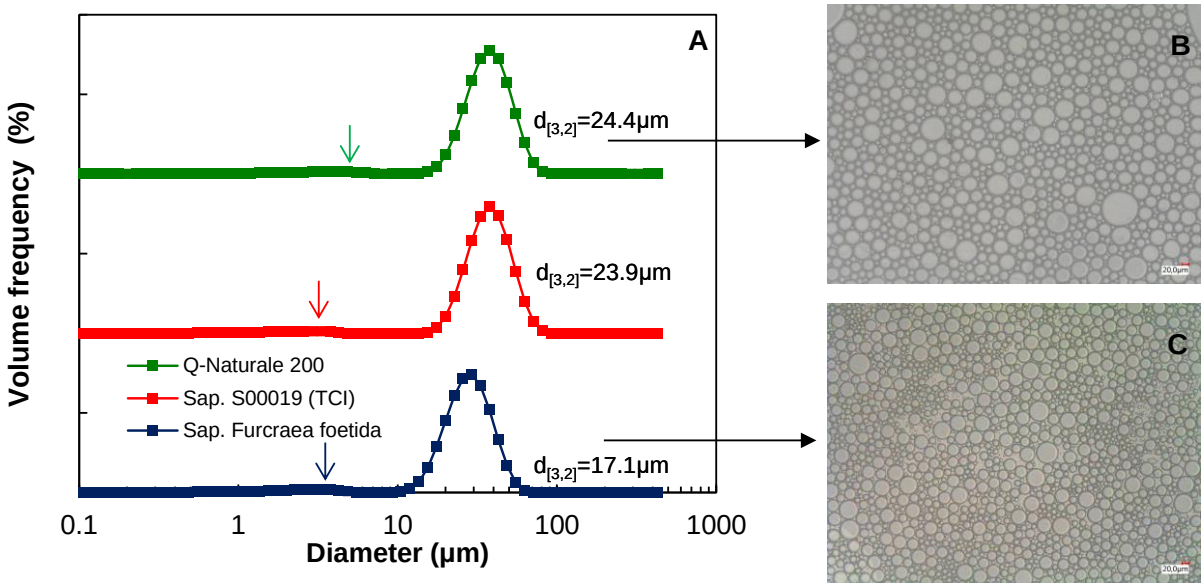


Figure 6. A) Droplet size distribution of prepared emulsions using different saponins in the 1wt.% Saponin/Isopropyl myristate/0.01M $NaCl_{(aq)}$ system (f_w=0.5). B) Observation of Q-Naturale and FF emulsion (C) using an optical microscope. Red bar indicates 20µm.

The concentration of surfactant is an important parameter into the formulation of emulsions. **Figure 7** shows the influence of saponin FF concentration on influence on $d_{(3,2)}$ and $dv_{(0.5)}$. As expected, when increasing the FF concentration the droplet size decreases by a large and fast coverage of the oil/water interface. An asymptotic behavior is reached in the vicinity of 0.5%, under the emulsification conditions, this concentration is enough to cover the interface and the excess of saponin remains in the the continuous phase. In order to compare the role of FF as emulsifier with a surfactant of same PIT-slope, **Figure 7A** shows the droplet size for emulsions formulated with different concentrations of Tween 40. At 1 wt.%, the size obtained with the polyethoxylated surfactant is slightly lower. However, when the concentration diminishes until 0.05 wt.% the difference increases and the size is higher for the emulsions with Tween 40.

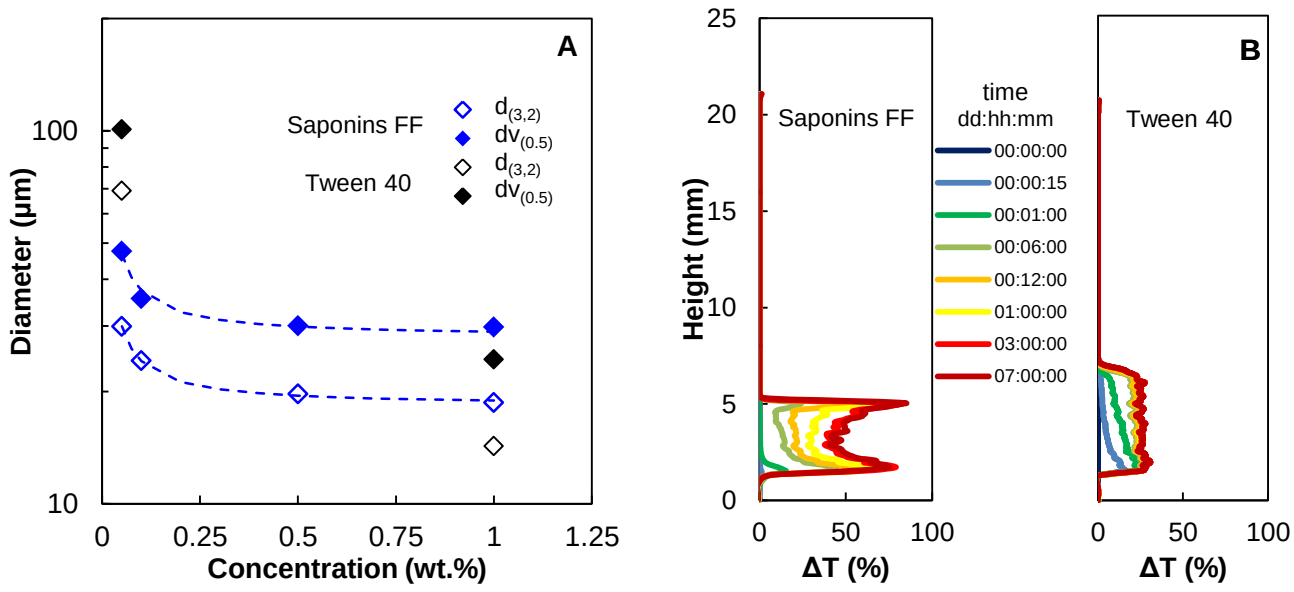


Figure 7. A) Influence of Saponins FF and Tween 40 concentration on the mean droplet diameter ($d_{(3,2)}$) and volume diameter $dv_{(0.5)}$ for Surfactant/IPM/Water emulsion at f_w=0.5. B) Delta Transmittance (ΔT) versus sample height and time at 25°C and for 0.05%Surfactant/IPM/Water emulsions at f_w=0.5.

Figure 7B show the delta transmittance (ΔT) measured at each height at different times for emulsions formulated with saponins FF and Tween 40 at 0.05wt.%. ΔT indicates the difference of the transmittance of the sample compared to the signal at t=0. Figure 7B show that both emulsions present a clarification phenomenon with time (high ΔT signal in the bottom zone of the tube). Comparing the profiles at the same time, the clarification is faster for the Tween than for the FF saponin, as expected for the higher size of their droplets at this concentration. Even if both emulsions have the same water fraction, the height of the clarified aqueous phase is slightly lower in the FF saponin emulsion. No coalescence is observed nor in transmittance nor in backscattering profiles.

The influence of the water fraction was also studied, changing from f_w = 0.5 to more "common" formulations namely f_w = 0.3, 0.7 and 0.9. The emulsion with a higher proportion of oil (f_w =0.3) does not present nor coalescence nor creaming for 7 days (figure SI4 on the supplementary information). The high content of internal phase increases the viscosity of the emulsion [49], decreasing the creaming phenomena observed for the other emulsions with lower content of oil. The size of these emulsions are similar to the system at f_w = 0.5 represented in **Figure 7A** (with $d_{(3,2)}$=15.1µm for f_w = 0.3, 14.5µm for f_w = 0.7 and 15.3 µm for f_w=0.9). The fact that the droplet sizes are equivalents for the sample with the higher and the lower amount of dispersed oil, indicates that the concentration of 1 wt.% of saponin is enough to fully cover the surface of the generated droplets at f_w = 0.3, and that it is largely in excess when the oil content is lower as in the samples at f_w = 0.7 and f_w = 0.9. This result confirms the asymptotic behavior observed in **Figure 7A** when f_w = 0.5.

In order to prevent the creaming phenomena, the emulsification protocol could be optimized to reduce the droplet. At a water fraction of 0.9, and the same concentration of FF saponins (1 wt.%), a nanoemulsion ($d_{(3,2)}$=200nm) can be obtained using ultrasonic sonotrode for 2 minutes. The size is clearly lower that the obtained with Ultraturrax (see figure SI5 on the supplementary information) and there is no creaming nor coalescence in 7 days. At this concentration using other stirring methods (high-pressure homogenizer [50] or microfluidizer [48]) nanoemulsions with the approximately the same size (200-250 nm) have been also reported in literature with QS, Tea saponin and Q-Naturale 200V.

3.3.2 Foaming properties

The ability of the 3 saponins to produce and stabilize the foam was investigated. In addition, Tween 40 and a commercial sodium laureth sulfate (Texapon N70) were also studied. The Tween 40 by its PIT-slope identical to the FF and the Texapon N70 by its well-known foaming properties that make it a typical ingredient in shampoo formulations [51]. All surfactants were tested at a concentration equal to 2 times its CMC (the foaming is maximum at concentrations near or higher than CMC [52]). The CMC values for Tween 40 and Texapon N70 are those reported by Ghosh [53] and Fieber [54], respectively (the weight concentrations for all experiments are indicated in table 3). **Figure 7** shows the foaming profile of the FF saponin and Texapon N70. This profile includes the initial period of time when the flow of air passes into the 50mL of surfactant solution until the total height (foam+liquid) of 180mm is reached. Then the stability is followed for 1200 seconds. The others saponins and Tween 40 profiles are not shown in the same figure to maintain its clarity.

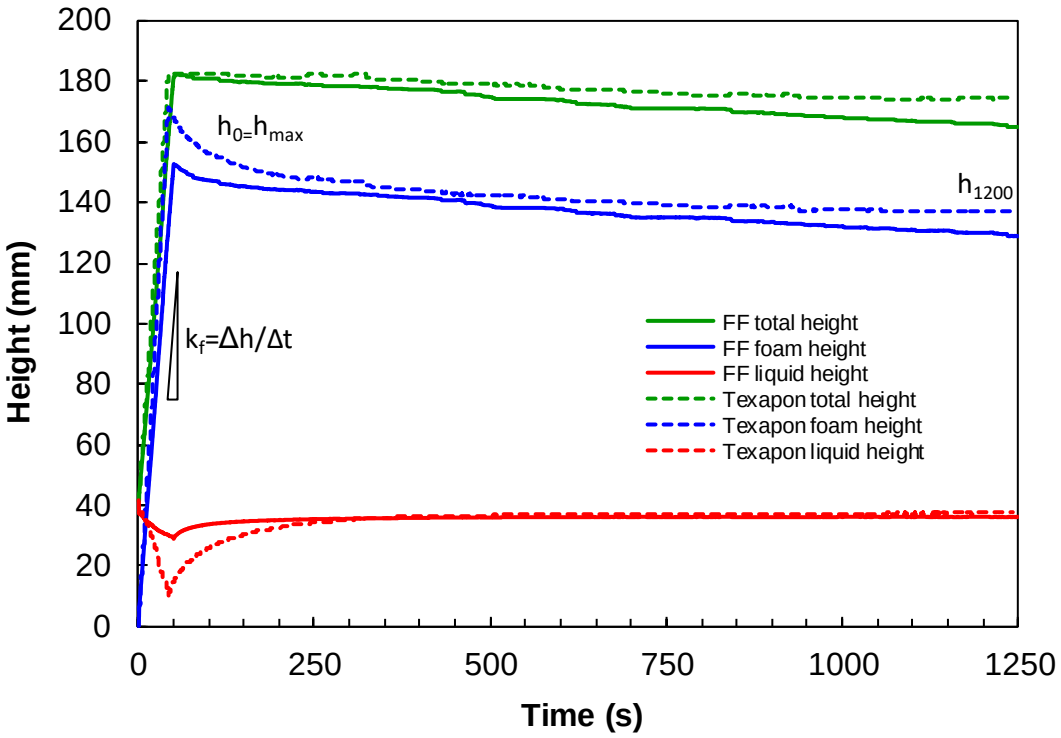


Figure 8. Foaming profile, height (mm) vs. time (s) for FF saponin (0.048 wt.%) and TexaponN70 (0.054 wt.%) at 2CMC.

The kinetics of the foam formation is quantified by the k_f parameter, the speed in which the maximum height of foam is reached, as schematized in **Figure 8**. **Table 2** contains all the parameters for the 3 saponins. The time required to reach the initial total height are comparable for the three saponins and the k_f constants are similar. For the Tween 40 the value is lower and for the Texapon N70 slightly higher, indicating that the foamability decreasing order is:

Texapon N70 > Saponin S0019 ≈ Q-Naturale 200 ≈ Saponin FF > Tween 40

However, their foam densities are different and the Texapon N70 and the Saponin from TCI incorporate much more liquid than others surfactants and these foams present the smaller size of bubbles at the beginning of the study. Indeed, when the total height of 180mm was reached, the difference on the foam density is easily pointed out in the liquid height of Texapon N70 that present deepest minima compared to the FF saponin (red dotted and continuous line in **Figure 8** for Texapon and FF saponin, respectively).

Table 2. Foam characterization. Foaming speed (k_f), foam density, foam stability at 1200s and average size of droplets when the height of foam is maximal (t=0) and at the end of the 1200s.

Surfactants	**Concentration (wt.%)**	**k_f (mm/s)**	**Foam density at h_{max}**	**Foam stability FS_{1200}**	**R_0 (µm²)**	**R_{1200} (µm²)**
Saponins *Furcraea foetida* (FF)	0.048	3.1±0.1	9±1	85.1±0.8	116±9	270±60
Saponin S0019	0.086	3.32±0.06	15±1	89.1±0.5	76±14	124±26
Q-Naturale 200	0.0052	3.15±0.02	6±1	92±1	174±40	264±75
Tween 40	0.0059	2.6±0.2	3.1±0.4	8±2	236±21	n.d.

Texapon N70	0.054	4.0±0.3	20±1	80±1	70±2	468±53

Concerning the stability, the 85.1% of the initial FF foam still remains after 1200s, a slightly high value than obtained with the anionic surfactant (80%) and considerably higher than the obtained with Tween 40 (8%). The decreasing order of stability is:

Q-Naturale 200 ≈ Saponin S0019 > Saponin FF > Texapon N70 >> Tween 40

The average size of the bubbles was followed at a height of 100 mm and it evolves from 116 (at t=0) to 270 μm (at t=1200s) for the FF saponin. The increase on the size of bubbles is slightly higher than for the other two saponins but it is considerably lower than the change quantified to the Texapon N70. For Tween 40, the measure at 1200s was impossible because there is no foam at the fixed height. The big difference on the mechanism of stabilization in foam surfaces between typical ionic and non-ionic surfactants is well stablished in literature [55]. For ionics, the stability is due to the electrostatic repulsion and for non-ionics via steric repulsion, needing different levels of surface coverage to get the same effect. The good foam stability properties of some saponins have been ascribed to their "high resistance to gas transfer of the saponin adsorption layers" [56]. Once again, the diversity of origin of the different saponins (and compositions) shows different behaviors [28]. However, the properties of foam formulated with FF are similar to those measured for the other two commercial saponins and the slightly ionic behavior determined by the PIT-slope could also be at the origin of the good foaming behavior.

4 Conclusion

The interest on new sustainable surfactants is growing in order to substitute petrochemical synthetic surfactants. Saponins are one of the most interesting alternatives and this work study the extract from *Furcraea foetida* as a new source of these surfactants from as a by-product of waste from the production of fibers. The described extraction process is easily reproducible on a large scale for future industrial applications. The solvents can be recycled after each extraction and reused. The most important saponins and flavonoids in the samples were described. Surface tension of FF extract allows determining the CMC (0.025 wt.%) in the expected range of those reported in literature. The hydrophilicity-lipophilicity behavior for FF and two commercial saponins (QS) was determined by the PIT-slope method and all saponins are hydrophilic: PIT slope Q-Naturale 200V > *FF* > S0019 (TCI). This method confirms also the ionic character of some compounds present in these samples, and for Q-Naturale 200V the conductivity-temperature profiles, when mixed with the $C_{10}E_4$/n-octane/0.01M NaCl system, presented a behavior comparable to well defined ionic surfactants, even if its PIT-slope value is close to high hydrophilic commercial polyethoxylated surfactants as $C_{12}E_{10}$. The PIT-slope of FF is identical to the value reported for Tween 40. The increasing conductivity and the decrease of pH when increasing FF saponin concentration indicate the presence of ionic compounds of acid character.

The surface properties of saponins were studied in dispersed systems: O/W emulsions and aqueous foams were formulated with all samples and compared with common benchmarks in these applications. Increasing the concentration of the FF saponin diminishes the size droplet of the emulsion at f_w=0.5 but for concentrations higher than 0.5% wt. the size remains identical indicating a saturation at the interface. At low concentrations (0.05% wt.), the size droplet of the FF saponin emulsion is lower than the Tween 40 and the clarification is slower. The good properties, at very low concentrations, indicate the high potential of FF saponins used as emulsifier. If all saponins are compared at the same concentration and water fraction (1% wt. / f_w=0.5) their stability and size are similar. When the water fraction changes until 0.3, very stable emulsions without clarification are obtained. Foaming properties of FF saponins are similar to those of other saponins and even more stables than those obtained with sodium laureth

sulfate (Texapon N70). The decreasing order of foam stability is Q-Naturale 200 ≈ Saponin S0019 > Saponin FF > Texapon N70 >> Tween 40. The smaller initial size of foam bubbles is obtained with Saponin S0019 (comparable to Texapon N70), probably due to the higher foam initial density. FF is a promising source of saponins with emulsifier and foaming properties as good as those described for commercial saponins. Moreover, toxicity and organoleptic properties must be studied to extend the application of these saponins in food and cosmetic domains.

ACKNOWLEDGMENTS

L'association Universitaire Francophone (AUF) is thanked by financing the travel of TR in Lille, France. Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Hauts-de-France, and FEDER are acknowledged for supporting and funding partially this work. We are grateful to Yves Koidjane who formulated and characterized the emulsions by ultrasound during his Master internship.

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