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Quillaja Triterpenic Saponins – The Natural Foamers

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Introduction

Saponins are natural surfactants found in many plants, especially those growing in desert climates. Saponins are also present in small amounts in some vegetal foods, such as soybeans and peas. Their industrial application is rapidly growing, firstly, under the pressure of the 'green wave', but also for their specific properties, which sharply differentiate them from common synthetic surfactants. The two major commercial sources of saponins are Yucca schidigera, which grows in the arid Mexican desert country of Baja California, and Quillaja saponaria (soapbark tree), found in arid areas of Chile. Saponins exhibit surfactant properties because their structures contain both water-soluble and lipid-soluble components. They basically consist of a lipophilic nucleus, having either a steroid or triterpenoid structure, with one or more side chains of hydrophilic carbohydrates (glycosyl chains). Yucca saponins have a steroid nucleus (steroidal saponins), while the quillaja saponins have a triterpenoid nucleus. Quillaja (synonyms: bois de Panama, Panama bark, quillai, Quillay bark, soapbark) extracts are obtained by aqueous extraction of the milled inner bark or wood of pruned stems and branches of Quillaja saponaria Molina (family Rosaceae), which is a large ever green with shiny, leathery leaves and a thick bark, native to China and several South American countries, particularly Bolivia, Chile and Peru. The word 'quillay' is derived from the native Mapuche word 'quillean' that means 'to wash'. Indeed, Quillaja bark has been used as a shampoo in Chile for centuries, while Native Americans used yucca to prepare soap.

As a consequence of their surface-active properties, saponins are excellent foaming agents, also forming very stable foams. Yucca and Quillaja extracts are used in beverages, such as root beer and slurpies, to provide the foamy »head« **(Fig. 1)**.
Because of their surfactant nature, they are also used industrially in mining and ore separation, in preparation of emulsions for photographic films, and, extensively, in cosmetics, such as cleansing formulae. In addition to their emollient effects, the antifungal and antibacterial properties of saponins are important in cosmetic applications.

Other Cosmetic Uses

Saponins and sapogenins have been reported as bioactive ingredients in cosmetic formulations, with claims related to the delaying of skin aging process (1, 2) and acne prevention (3). Oleanolic acid, one of the most common triterpene saponins' aglycone, has been reported to possess anti-viral (anti-HIV), anti-inflammatory, hepatoprotective, anti-ulcer, antibacterial, hypoglycaemic, anti-fertility and anticariogenic activity (4). The same properties have been demonstrated for betulinic acid and its derivatives (5). Due to their surface active properties, saponins are being utilized as surfactants in cosmetic cleansing products such as shower gels, shampoos, foam baths, hair conditioners and lotions, bath/shower detergents, liquid soaps, baby care products, mouth washes, and toothpastes (6-8). Commercially available natural surfactants containing saponins include Juazarine from the bark of *Zizyphus joazeiro* tree (9) and horse chestnut saponins (10).

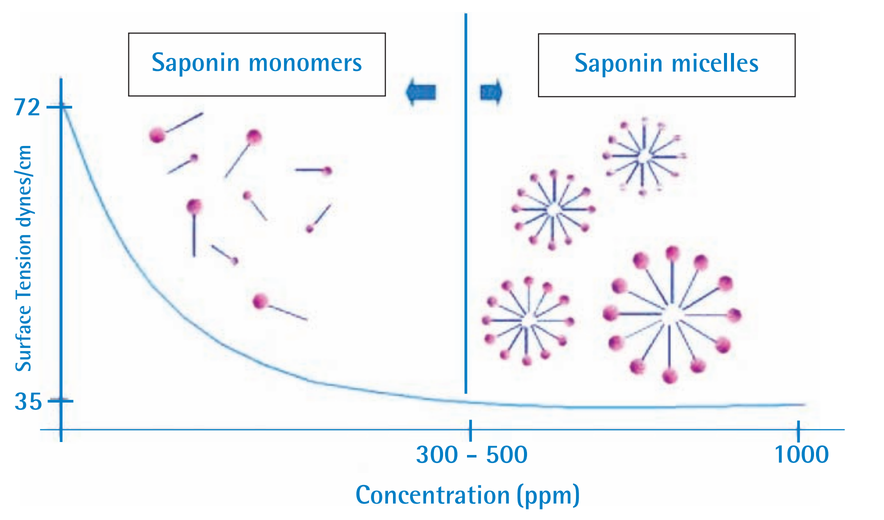

Fig. 1 Micelle formation. Correlation between surface tension (dynes/cm) and Quillaja saponins concentration (ppm)

Composition

Quillaja extract contain over 100 triterpenoid saponins, consisting predominantly of glycosides of quillaic acid. Polyphenols and tannins are also major components. Some simple sugars and calcium oxalate are also present (11, 12) in the extract. Quillaja triterpenic saponins are non-ionic surfactants, resistant to salt, heat, and extremely stable to acid pH. They consist of a five-ringed quillaic acid backbone with small carbohydrate chains, consisting of two to five sugar units, attached at the 3´ and 28´ carbons of quillaic acid and are frequently branched (13) **(Fig. 2)**.
Attached to the first sugar (fucose) unit of the carbohydrate chain, at the 28´ position, there is a 18 carbon atoms acyl chain with a small carbohydrate chain at its terminal end, which consists of one or two sugar units. The substitution of different sugar chains gives rise to at least 50 different types of quillaja triterpenic saponins. Their average molecular weight is 1800 - 2000 Dalton. Below 200 - 500 ppm concentration, saponins exist as monomers. Above such level, they aggregate to form micelles, with an apparent molecular weight of approximately 100.000 Dalton.

Cosmetic Grade

In order to be suitable for cosmetic uses, quillaja extracts need a careful purification. Andean QD ultra is a spray-dried purified aqueous extract of the Chilean Soap Bark Tree (Quillaja Saponaria Molina), with an average composition as follows:

Moisture content	2.0 – 7.0%
Fibre	0.01 – 0.5%
Proteins	3.5 – 7.0%
Ash	6.5 – 12.0%
Fats	0.01 – 0.5%
Carbohydrates	73.0 – 87.94%

It is a light-beige free-flowing powder. The pH of a 10% aqueous solution of saponins is around 4. The aqueous solution has a yellow-brown appearance.

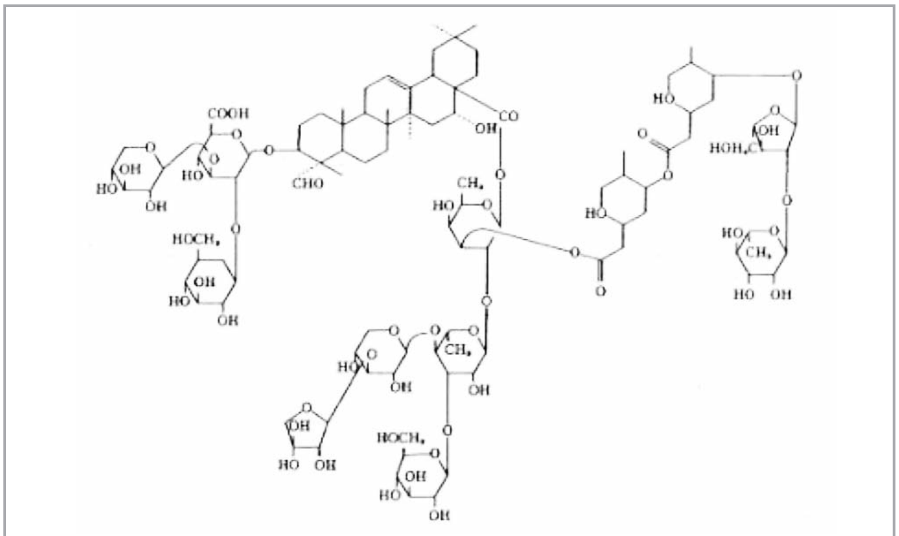

Fig. 2 Chemical structure of quillaja saponins

Aims of the Study

The aims of the study were to evaluate the compatibility, interactions and performances of the quillaja extract, when formulated with common cosmetic ingredients, in order to identify all the possible applications of the raw material in finished cosmetic products and the key characteristics of such formulations. Particular attention was kept to mouth cleansing products, where the need for the replacement of the traditional synthetic surfactant sodium laurylsulphate is fuelled by the increasing awareness of its potential harmful effects on the mouth mucosa.

Compatibility Study

Alkali
As said before, triterpenic saponins solutions are acidic. Their neutralization with several alkali like triethanolamine, sodium hydroxide or Arginine, does not modify their stability. Only a slight and reversible intensification of the brown colour is observed. This shade vanishes as soon as pH is brought back to the initial values, e.g. with lactic acid.

Ethanol
10% saponins solutions maintain their transparency by successive ethanol addition up to a maximum of 20%. Between 20% and 30% a progressive opacity increase is observed.

Interaction with hydrotropes
10% saponins solutions have been prepared. The following ingredients have been added, up to 5% concentration: Urea, Betaine, Inositol, and Glycerine. Sorbitol, Propylene Glycol, Maltitol were added up to 20%. In all these cases, the solutions appearance was kept unchanged; it is only perceived a light worsening of skin feel (drag) with Glycerine, while a slight improvement (emollient touch) was perceived in the case of Inositol.

Foam Formation

The capability to generate foam from a solution of the above purified quillaja triterpenic saponin and by its blends with common surfactants has been evaluated. Blends were prepared in variable ratios common surfactant:saponins, while the TWS (total washing substances) level has always been kept constant at 0.5%. The synthetic surfactants used were:

- Sodium laureth sulphate (SLES);
- Coco Glucoside (CG);
- Sodium Cocoamphodiacetate (SCD)
- Sodium Sulfosuccinate (SSC)

Binary blends and ternary blends have been prepared.

Method

A 100 mL aq solution @ 0.5% TWS, kept in a 400 mL beaker and thermostated to 25 °C, is homogenized (Silverson) for 1' at maximum speed with the homogenizer bearing a holed sieve for emulsions, with circular holes. The whole solution and foam are carefully poured in a 250 mL cylinder, internal diameter 35 mm, and left standing for 1' (t°). Then, the foam column is measured (in mms) with the aid of a rule, so determining 'h°'. The reading is repeated after 5' (t') so determining h'.

Foam Results

The values at t° (h°) and at t' (h') are here reported (**Table 1a, 1b, Fig. 3**, and **Table 2a, 2b, Fig. 4**). Average error of the measure is 5 mms. In addition, the relative foam stability values (% stability), are calculated as the percentage ratio between h' and h°.

From the above results, it is evident that purified quillaja triterpenic saponins, when used alone, have an average foaming power which is about 40% lower than for most high-foaming surfactants. Indeed, this is a common feature of mild surfactants. When blended at decreasing % with the base surfactants, an inverse

Foam height / stability			
Saponin / SLES	h_0	h_1	%
100	145	75	52
80:20	160	105	66
50:50	225	175	78
20:80	225	180	80
0	235	195	83

Table 1a

Foam height / stability			
Saponin / CG	h_0	h_1	%
100	145	75	52
80:20	170	120	71
50:50	185	135	73
20:80	215	175	81
0	235	185	79

Table 1b

Foam height / stability			
Saponin / SCD	h_0	h_1	%
100	145	75	52
50:50	175	120	69
0	205	155	76

Table 2a

Foam height / stability			
Saponin / SSC	h_0	h_1	%
100	145	75	52
50:50	165	105	64
0	190	130	68

Table 2b

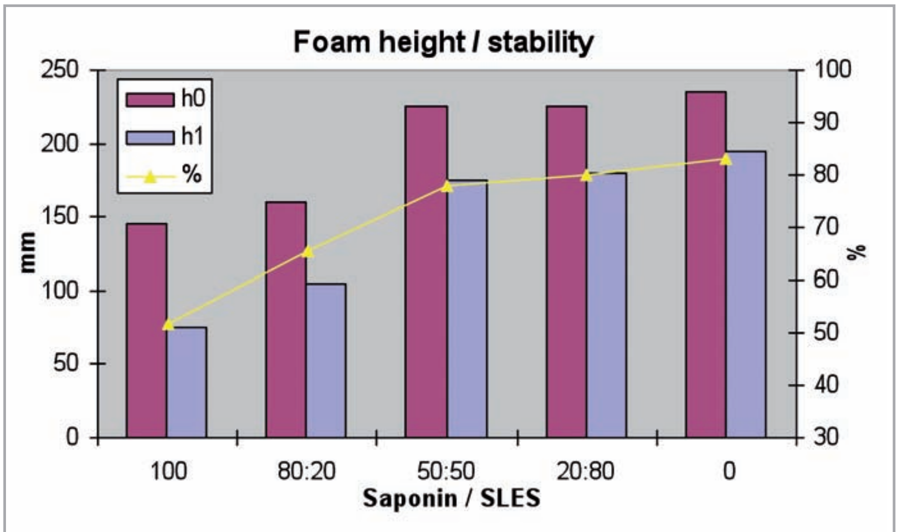

Fig. 3 Foam height and foam stability of different binary mixtures of Saponins and SLES

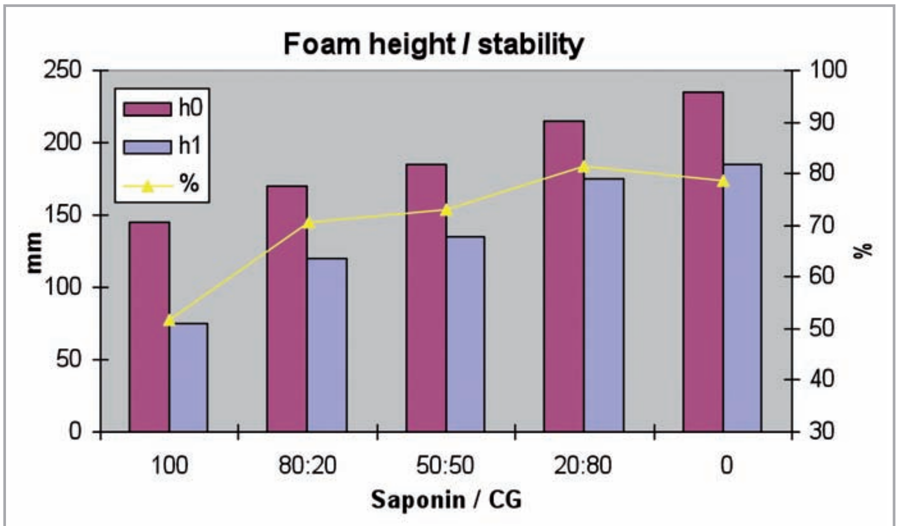

Fig. 4 Foam height and foam stability of different binary mixtures of Saponins and Coco-Glucoside

proportionality is measured between its amount and the foaming power. Nevertheless, it is interesting to note that the blend prepared with coco-glucoside (CG), in the ratio 80:20, has foaming power better than when it was prepared with SLES. Foam quality remains in all cases, optimal, i.e. small, homogeneous bubbles.

■ Ternary Blends

One example of optimized ternary blend is here reported. The interesting behaviour of saponins with alkyl glucosides can again be observed **(Table 3)**.

Foam height / stability			
Mixture	h_0	h_1	%
Saponin	145	75	52
Sa60:CG20:SCD20	175	125	71
Sa60:SSC20:SCD20	175	115	66

Table 3

■ Compability with Natural and Synthetic Polymers

Solutions containing 10% purified triterpenic saponins and a series of natural and synthetic polymers were prepared, in order to verify their compatibility and thickening potential towards saponin solutions. The amount of polymers in solution was always kept at 1% (total solids). The polymers selected on the basis of their use frequency in cosmetic formulations were:

1) Acrylates/C10-30 alkyl acrylate crosspolymer (Pemulen TR-1);
2) Acrylates/C10-30 alkyl acrylate crosspolymer (Pemulen TR-2);
3) PEG-150/Decyl Alcohol/SMDI Copolymer (Aculyn 44)
4) PEG-150/Stearyl Alcohol/SMDI Copolymer (Aculyn 46)
5) Chondrus Crispus Extract (carrageenan – Viscarin PC 389)
6) Cellulose Gum (Blanose 7HF)
7) Xanthan Gum (Comixan ST/HV)
8) Hydroxyethyl Cellulose (Natrosol 250 HHR)
9) Hydroxypropyl Methylcellulose (Tegocell HPM 4000 and 50)
10) Carbomer (Carbopol Ultrez 10)

Viscosity values (mPa.s)				
Polymer	1% aq polymer solution		+ Sap 10%	
	2,5 rpm	5 rpm	2,5 rpm	5 rpm
Xanthan Gum	12.000	6.000	16.000	9.000
Acrylates/C10-30 alkyl acrylate crosspolymer (Pemulen TR1)	76.000	44.000	16.000	9.000
Acrylates/C10-30 alkyl acrylate crosspolymer (Pemulen TR2)	80.000	50.000	40.000	26.000
Chondrus Crispus Extract	84	92	76.000	40.000
Hydroxyethyl Cellulose	3.800	3.300	4.800	4.000
Cellulose Gum	1.400	1.320	800	800

Table 4

Viscosity results have been compared with master gels prepared without saponins **(Table 4)**.
Unsatisfactory results of some blends (3, 4, 9 and 10) are due to incompatibility and are not reported here. Some molecules show some decreased thickening effect, some others, like Xanthan Gum, hydroxyethylcellulose and, outstandingly, Carrageenan, show interesting enhanced thickening effect. At the light of the interesting results obtained with the two natural polymers Xanthan Gum and Chondrus Crispus Extract, lower (and higher) amounts of saponins have been tested, while keeping constant the polymer amount **(Table 5 and 6, Fig.5)**. All solutions are being submitted to stability testing.

Viscosity values Chondrus Crispus Extract 1%		
Saponin %	2.5 rpm	5 rpm
0	84	92
1	16.000	10.000
5	20.000	16.000
10	76.000	40.000
15	1.900	1.300

Table 5

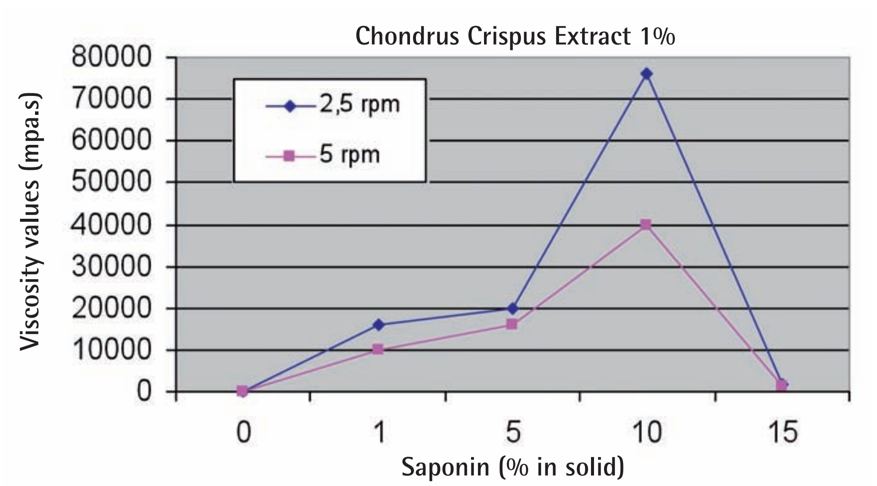

Fig. 5 Viscosity values at 2,5 and 5 rpm of solutions with Chondrus Crispus Extract at 1% at different percentages of Saponins

Viscosity values Xanthan Gum 1%		
Saponin %	2.5 rpm	5 rpm
0	12.000	6.000
1	10.000	6.000
5	14.000	9.000
10	16.000	9.000
15	18.000	10.000

Table 6

Thickening Results

The tests clearly show that there is the creation a positive synergic interaction between natural polymers and Quillaja triterpenic saponins in aqueous solution. In particular, in the case of Carageenan, saponins dramatically increase the thickening power of the polymer. For this reason, the presence of the polymer could somehow affect the foaming power of saponins solution or their stability has been verified. While considering gels at 10% purified quillaja saponins and 1% Xanthan Gum or Chondrus Crispus Extract, the foam production test, at the same concentration as above was repeated. Results are shown in **Table 7**.

Foam height / stability			
Saponin	h_0	h_1	%
alone	145	75	52
+ Chondrus Crispus Extract	140	115	82
+ Xanthan Gum	143	115	80

Table 7

The addition of both polymers noticeably increases the foam stability, without decreasing its height and quality.

Interactions with Salts and Organic Thickeners

Mineral salts have a thickening effect of many surfactant solutions. 10% aqueous solution of saponins where the following salts have been added, up to 4% concentration: NaCl, KCl or $MgCl_2$, did not show any noticeable viscosity change.

No viscosity changes of the 10% Saponins solution took place with the following organic thickeners: Cocamide DEA, PEG-120 methylglucose dioleate, PEG-90 glyceryl isostearate – Laureth-2, all used at 3% active concentration.
In conclusion, quillaja triterpenic saponins require thickening polymers in order to reach quite interesting flow properties and rheology in cleansing systems where saponins are used as the primary surfactant.

Compatibility with Pigments and Powders

After preparing the standard solutions of saponins at 10%, its powder wetting capability has been tested by introducing some pigments or other insoluble powders at 10%. Pigments and powders are placed in a beaker and left mixing by magnet, for 5'. Successively, dispersions have been evaluated visually and by optical microscope, in comparison with the dispersion made in water but without saponins. The tested ingredients were:

Inorganic Pigments
Titanium Dioxide
CI 77492
(Iron Oxide – A407 Tudor Willow)
CI 77491
(Iron Oxide – A402 Tudor Rosewood)

Fillers/ Mineral Powders
Hydrated Silica (Tixosil 73)
Silica (Aerosol 200)
Dicalcium Phosphate
Dicalcium Phosphate Di-hydrate

Results

Pigments
Dispersions of mineral pigments result much finer when saponins solution is used. Such difference can be clearly be detected with the microscope, but is also evident without any instrument. These results will be very useful for the preparation of foundations, which usually contain 10% pigments.

Fillers/ Mineral Powders
On the contrary, the dispersions of powders used as abrasives in toothpastes result worse than in water, when saponins are dissolved. In particular, with anhydrous Di-calcium Phosphate, Di-calcium Phosphate Di-hydrate and Hydrate Silica, a higher amount of aggregates is visible. Moreover, saponins reduce the viscosity of Silica gels. Nevertheless, the viscosity of silica gels recovers by leaving the dispersion standing, so to deaerate. As the amount of saponin in the tested solutions was comparably high, in relation to commonly used laurylsulphate, we repeated the trials with lower saponins amount (0.5%, 1% and 2%). In all cases, the quality of dispersions increases by decreasing the amount of saponins. Only in case of Silica, the initial thinning effect is kept even using 0.5% saponin. In successive trials, it has been verified that pigment dispersions are noticeably improved when pigments are previously wet by 20% w/w glycerine. Such improvement is more easily realised with Dicalcium Phosphate and Hydrated Silica.

Solubilising of Sparingly Soluble Ingredients

Because of their special structures and affinity for vegetal moieties, the solubilising power of purified Quillaja triterpenic saponins toward sparingly soluble ingredients or vegetal extracts has been verified. In **Table 8** the amount (as total solids) of saponins used is reported, together with the INCI names, the amount of tested ingredients and the results obtained when comparing the same solutions without saponins.
It is evident the capability of saponins to induce solution or easier dispersion of many molecules characterized by molecular structures made of aromatic rings, both alone or condensed, with a maximum condensation number between 2 and 3.
As a special result of these trials, it was noticed that the 25% solution of saponins with 5% tocopherol has a particular behaviour. Indeed, an opaque gel is formed, that gives stable milk when diluted in water.

Applications

On the basis of the above described properties and characteristics in simple systems, the possible application of Quillaja triterpenic saponins as active/functional ingredient in complex blends has been investigated. For this reason, the effect of purified saponins addition in cosmetic preparations has been realised, and the most suitable dosage has been inspected.

Solubility			
Ingredients (w/w %)	Saponins (w/w %)	Results	Results/ no saponins
Allantoin (0.6)	5	precipitate	precipitate
Salicylic acid (0.25)	4	partially soluble	precipitate
Glycyrrhetinic acid (0.1)	4	precipitate	precipitate
Azelaic acid (0.2)	4	precipitate	precipitate
Boswelia Serrata (0.4)	4	easier wetting precipitate	precipitate
Coleus Forskohlii Root Extract (0.1)	4	partially soluble	precipitate
Quercetin (0.1)	4	easier wetting precipitate	precipitate
Catechin (0.6)	4	soluble	precipitate
Rosmarinus Officinalis Extract (0.4)	4	precipitate	precipitate
Biotin (0.08)	4	partially soluble	precipitate

Table 8

Formulations

Phase	Trade Name	INCI Name	% w/w
A	Protelan LS 9011 (30%)	Sodium Lauroyl Sarcosinate	5.00
	Rewomid IPP 240	Cocamide Mipa	1.00
	Octopirox	Piroctone Olamine	0.20
B	Plantacare 818	Coco Glucoside	18.00
C	demin. Water	Aqua	51.00
	Inositol	Inositol	1.00
	Natrlquest E30	Trisodiummethylenediamine Disuccinate	0.20
D	Styleze W10	Polyquaternium-55	0.40
E	Andean QD Ultra (Sol. 25%)	Quillaja Saponaria Extract	8.00
F	Setacin 103 SP (30%)	Disodium Laureth Sulfosuccinate	8.00
G	Rewoderm LI S 80	PEG-200 Hydrogenated Glyceryl Palmate, PEG-7 Glyceryl Isostearate	4.00
	Oxetal VD 92 (80%)	PEG-90 Glyceryl Isostearate	1.00
	Parfum	Parfum	0.60
H	Nipaguard SMG	Sodium Hydroxymethylglycinate	0.80
I	Lactic Acid	Lactic Acid	0.80
			100.00

Anti-Dandruff Shampoo

Phase	Trade Name	INCI Name	% w/w
A	dem. Water	Aqua	23.59
	Viscarin PC 209	Chondrus Crispus Extract	1.00
A1	demin. Water	Aqua	5.00
	Sodium Saccharin	Sodium Saccharin	0.25
	Sodium Monofluorophosphate	Sodium Monofluorophosphate	0.76
	Sorbitol (Sol. 70%)	Sorbitol	25.00
	PEG-8	PEG-8	4.00
B	Tetrasodium Pyrophosphate	Tetrasodium Pyrophosphate	1.75
	Tetrapotassium Pyrophosphate	Tetrapotassium Pyrophosphate	1.75
C	Tixosil 73	Hydrated Silica	7.00
	Tixosil 43	Hydrated Silica	7.00
	Aerosil 200	Silica	1.00
	Sodium Bicarbonate	Sodium Bicarbonate	12.00
D	Sorbitol (Sol. 70%)	Sorbitol	2.00
	A310 Tudor Aspen	Titanium Dioxide	0.50
E	demin. Water	Aqua	4.00
	Andean QD Ultra	Quillaja Saponaria Extract	2.00
F	Aroma	Aroma	1.20
	Irgasan DP 300	Triclosan	0.20
			100.00

Anti-Plaque Toothpaste

Conclusions

Purified Quillaja triterpenic saponins seem to crown the dream of modern formulator, aimed to identify skin compatible, environmentally friendly, surfactants having a low toxicity profile. Beside applications in cleansing systems, the most interesting results appear in toothpastes and mouthwash formulation, where the foaming profile and the mucosa-friendly behaviour open a new horizon to the formulation of mouthcare formulation with a low irritation profile. On the other side, the special properties given to natural thickeners and the solubilising properties toward complex organic molecules suggest a wide range of experiments for exploring the apparently unlimited number of cosmetic application where surface interactions phenomena are involved. Innovative application for emulsion, were synthetic emulsifiers are being replaced by Quillaja triterpenic seems the most promising future steps.

References

(1) *Yoo B.H., Kang, B.Y., Yeom, M.H., Sung, D.S., Han, S.H., Kim, H.K,* and *Ju, H.K.* 2003. Nanoemulsion comprising metabolites of ginseng saponin as an active component and a method for preparing the same, and a skin care composition for anti-aging containg the same. US Patent Application 2003/0 175315 A1

(2) *Bonte F., Meybeck, A.*, and *Massiot, G.* 1998. Method of treatment for combating the effects of aging on the condition of skin and hair. US Patent 5,770,223. *Brand, H.* and *Brand, E.* 2004. A weighty issue. Soap, Perfumery & Cosmetics Asia, March, 27-31

(3) *Bombardelli E., Morazzoni, P., Cristoni, A.*, and *Seghizzi, R.* 2001. Pharmaceutical and cosmetic formulations with antimicrobial activity. US Patent Application 2001/0046525 A1

(4) *Liu J.* 1995. Pharmacology of oleanolic acid and ursolic acid. J. Ethnopharmacol., 49: 57-68

(5) *Yogeeswari*, P., and *Sriram, D.* 2005. Betulinic acid and its derivatives: A review on their biological properties. Curr. Med. Chem., 12: 657-666

(6) Indena, 2005. Horse chestnut saponins. http://www.indena.com/pdf/cosmleaf.pdf, accessed 24/8/2005

Phase	Trade Name	INCI Name	% w/w
A	dem. Water	Aqua	56.55
	Xylisorb 300	Xylitol	1.00
	Vegetable Glycerin	Glycerin	3.00
	Melissa (water demin.)	Melissa Officinalis Distillate	2.00
	Hamamelis (water demin.)	Hamamelis Virginiana Distillate	2.00
	Glyceric Rosemary Extract	Rosmarinus Officinalis Extract	1.00
B	Viscarin PC 389	Chondrus Crispus Extract	1.00
C	Andean QD Ultra (Sol. 25%)	Quillaja Saponaria Extract	8.00
D	Plantacare 818 UP	Coco Glucoside	20.00
E	Ethanol (From Organic Wheat)	Ethanol	5.00
	Phenoxyethanol	Phenoxyethanol	0.40
	Olio Essenziale Lavanda Hybrida	Lavandula Hybrida Oil	0.05
			100.00

Biological Detergent Gel for Impure Skin

(7) *Olmstead M. J.* 2002. Organic toothpaste containing saponin. US Patent 6,485,711 B1

(8) *Brand, H.*, and *Brand, E.* 2004. A weighty issue. Soap, Perfumery & Cosmetics Asia, March, 27–31

(9) Anonymous, 2004. The fine line. Soap, Perfumery & Cosmetics, July:57

(10) equal to (6)

(11) *Güçlü-Ustündag O, Mazza G.* Saponins: Properties, Applications and Processing. Critical Reviews in Food Science and Nutrition, Volume 47, Issue 3, 2007, Pages 231 – 258

(12) http://lpi.oregonstate.edu/sp-su98/saponins.html accessed February 2009

(13) Quillaia Extracts, Type 1 and Type 2 – Chemical and Technical Assessment (CTA), First draft prepared by *Silvia Resnik*, © FAO 2004 6 1st JECFA

(14) *Bomford, R., Stapleton, M., Winsor, S., Beesley, J.E., Jessup, E.A., Price, K.R. & Fenwick, G.R.* 1992. Adjuvanticity and iscom formation by structurally diverse saponins. Vaccine, 10: 572–577

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