DEVELOPMENT OF A COSMOS SOLID EMULSION

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Abstract

Natural products are becoming a trend in the cosmetic market, due to a growing awareness and concern with the origin of these products. The certification of natural products, especially organic ones under the COSMOS signature preserves the integrity of the constituents, in an environmentally appropriate and safe for human health, expanding the concept of "green chemistry", guaranteeing the origin, and processing of the products, storage, manufacturing, packaging, etc. [1]. The objective of this study was to develop a moisturizing cosmetic emulsion according to COSMOS certification, in a new concept of solid cosmetic format. 59 different tests were carried out to optimise this emulsion, included variations in components and their amounts, following be evaluation of sensory aspects for each formulation. The final formulation contains components of Portuguese origin such as grape seeds oil from Douro Valley, olive oil and extract of by-products of acorn (*Quercus Ilex* L.) and essential oils of mandarin, geranium, coriander and cinnamon. The formulation has undergone accelerated stability tests with temperatures (40 °C /-12 °C). The pH, density and organoleptic characteristics were evaluate. The phenolic profile of acorn by-product (*Quercus ilex* L.) was performe by UHPLC-DAD-ESI-MS2. A questionnaire was applying to evaluate the acceptance after use of the moisturizing cosmetic emulsion. In stability tests, overall the formulation showed small color variations and less aroma intensity, maintaining hydration and solid state. The pH changes were from 4.68 ± 0.006 to 4.78 ± 0.05 and the density was maintaining at 0.73 kg/m^3. The polar extract of acorn by-product have as major compounds trigalloyl-HHDP-glucose, valoneic acid dilactone and gallic acid, known as antioxidants compounds. [2,3]. The essential oils bring beneficial properties to the skin and the aroma. In the post use of solid emulsion survey applied shown that "aroma" was the second point most valorised (47.6%), after "hydration" (90.5%). The results shown that the majority of participants (81.0%) were "very satisfied" or "satisfied" with the solid emulsion indicating the intention to use it if it is on the market (76.2%). This study highlights the research in reformulations from liquid to solid products, and the potential of using Portuguese raw materials such as acorn by-product (*Quercus ilex* L.).

Introduction

Our skin, also referred as cutaneous membrane, is our biggest organ and it is a very complex one. In its composition you can find two main layers: the dermis (the internal layer) and the epidermis (the external layer). In cosmetics, the epidermis is the primary target of skin-care products to enhance its complexion. This outer layer is constituted by two main cell groups: keratinocytes and dendritic cells and is known to be a stratified and scaled layer. In it we can find the Stratum Corneum (CS) responsible for protection functions such as substance transference between the skin's outside and inside and is considered the life barrier due to its restrict permeability and osmotic impermeability. Hydration is dependent on the CS hygroscopic properties and environmental humidity, as well as proportional to the Natural Hydration Factor (NHF) of the CS, usually lower on dry skins. Figure 1 shows the Corneocytes structure on a dehydrated skin, with a higher fissure count, which restraints the skin natural barrier functions. Lower hydration levels are usually associated with a fragile CS.

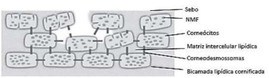

Figure 1: Corneocytes structure on dehydrated skin (Adaptation from Matos, 2019)

Besides restraining the skin barrier functions, the hydration levels influence the CS enzymatic activity, therefore having an impact on the descaling process (the keratinocytes transformation process into corneocytes and dead cells) and the natural hydration level.

Cosmetic hydration creams are used for dry skin syndrome treatment, in order to stabilize the skin's mildness, being also capable of prevent and repair defects on the skin barrier function. LODÉN, M. (2015). Usually, these products are emulsions of heterogenic systems of emulsifying agents' immiscible phases. The COSMOS natural and organic certification main objective is to uphold a higher standard of origin tracking and sustainability of the certified products.. Figure II illustrates the COSMOS certification seals.

Figure II: COSMOS natural and organic certification signatures; Certification seals, accessed at 05/01/2020

Materials

The development of the formulation took place in the work and industrial environment of a Portuguese company of biological cosmetics that has a range of biological and preferentially portuguese compounds, from emulsifying, emolying agents, conscious agents and many other compounds. parting for practices through the basic formulation provided and described in table 1.

Table 1: Base formulation (T1.1)

TEST T1.1	Components	%	TEST T1.1	Components	%
Oily phase	Lecithin	27,37%	Water phase	Glicerine	76,92%
	Karite butter	11,39%		Sodium PCA	54,55%
	Olive oil	2,01%		Water	97,83%
	Stearic acid	86,96%			
	Cetearyl alcohool	100,00%			
	Isoamyl laurate	60,00%	Cold phase	Tocopherol	99,91%
	Cocoa butter	50,00%		Blooming Summer EO (*)	93,75%
	Broccoli oil	17,25%			
	Fractionated coconut oil	19,66%			

(*) Blooming summer EO is a mixture of essential oils produced and marketed by the company where the work was developed.

Methodology

The starting point was the base formula (Table 1), supplied by the company, with distinction of the initial compounds with solid agents, such as cetearyl alcohol and stearic acid, separated by their respective phases (aqueous, oily and cold), with the objective of obtaining a solid phase for the hydration emulsion. The oily phase components were heated to 65°C - 75°C and after being fused together, the aqueous phase was added (50 - 60°C) initiating the homogenization process on a food processor at various speeds (150-300rpm) until the mix was at 50°C (± 5°C) temperature. Then the cold phase (thermosensible compounds) is incorporated via agitation for aprox. 5 minutes so the product can be transferred to silicone molds to rest for 24 hours.

- Sensory Tests

The sensorial characteristics measured were stiffness (A), crumbling (B), oiliness (C), skin absorption (D), spreadability (E) and, solid product residues (F) using two different scales. The first being from 0 (nullable or irrelevant) to 5 (high processing) and the second scale representing the formulation perfection degree with higher amplitude, ranging from 0 (nullable or irrelevant) to 10 (high processing)

- Stability Tests

The final product was analyzed for its organoleptic characteristics (color, odor, phase separation, texture and consistency), pH and density, before and after cycles with extreme thermal variations, remaining 24 hours in freezing at -12C and, 24 hours in a bath -water at 40°C (6 cycles for each thermal variation).

- Extraction of phenolic compounds from acorn by-products

The sample of by-products of the acorn, made available in fine and dry granules, comes from the holm oak plant of the species Quercus ilex L., constituted fundamentally by skins and fruit casing, and there may be remains of the fruit itself, traces of leaves and stems of the plant. The extraction of the phenolic compounds was carried out according to the method described by Ferreira et al. with adaptations. It was then reduced to fine powder and 5 g were extracted for 15 min using a 1:20 80% hydroalcoholic solution (5 g in 100 ml of water). The extract was filtered and the residue re-extracted two more times. The total filtrate (300 ml) was concentrated using a rotary evaporator at 37 ° C. (BUCHI Labortechnik AG, Flawil, Switzerland). The resulting fraction was frozen, lyophilized and kept under vacuum in a desiccator, in the dark, for subsequent use.

- Phenolic Compounds Identification

The phenolic profile of the polar extract of the acorn by-product (10 mg / mL) was determined by analysis in liquid chromatography (UHPLC-DAD-ESI-MS2) using an apparatus equipped with an Ultimate 3000 diode detector (Dionex Co., San Jose , CA, USA) and a Thermo LTQ XL mass spectrometer (Thermo Scientific, San Jose, CA, USA), following the method described by Afonso et al.42 Phenolic compounds were identified using standard commercial compounds whenever possible, or else , based on the interpretation of ultraviolet (UV) and mass spectrometry (MS and MS / MS) data, in addition to comparison with the literature.

- Questionnaire for the characterization of the skin's moisturizing emulsion after use

In order to assess the after use perception of the solid moisturizing cream to evaluate the points of greatest satisfaction and dissatisfaction of the volunteers and to understand the potential for acceptance of the developed solid cream, a questionnaire was applied online, with a sample of 21 volunteers, after daily use of the product for a period of 5 days, following the use instructions provided in an explanatory leaflet.

Results

The first formulation stage was based on the development of a stable solid base, that is, that the emulsion had a good texture, solidifying after the total homogenization of the compounds and cooling of the formulation, maintaining a good appearance and that it was moisturizing.The results of the tests developed in this first stage are described in table 3.

As can be seen, the first tests all presented some degree of solid residue, indicating a low rigidity of the product. As advances this degree has been reduced, in order to achieve a high degree of rigidity with no product residue. Tests were carried out with incorporation of starch in cassava starch, T2.2 and T3.2, 10% and 5% respectively, observing a high degree of crumbling in both final products, while the sample T2.1 and T3.1 (without starch) showed a lower degree of crumbling, but present, indicating that more compounds should be tested in the formulation.

The water had been added in different proportions and ways during the tests, either in its pure form or in lavender hydrolate, or even by the aqueous extract of acorn (Quercus ilex L.) and, even in the case of a solid emulsion , proved to be fundamental in the formulation, since the samples where water was not present, T13, T14, T15 and T16, there was less effectiveness of the emulsification process and, after application on the skin, a hydration effect was noted lower than desired, with a slight excess of oil, according to the results observed in table 3.

After achieving the best result for all aspects, as evidenced in the T41 test, a second step to improve the tests was carried out, as shown in table 4. In samples T45 and T46, two compounds stand out, the Olive squalene wax (T45) and Squalene-based olive wax butter (T46), which were incorporated in place of carnauba wax. (of stiffening properties). The results observed in the T45, were very promising and, the slightly high oiliness (grade 6) is of interest for a moisturizing emulsion. It is very stable and much easier to work with due to its melting point being lower than carnauba wax (the main hardener used until then), in addition to protecting the skin and preventing moisture loss, being also used in anti creams. -aging. [5]

The best result obtained was that of the T52.1 test, which obtained an average scale value (5) for all sensory parameters, with no degree of crumbling or product residues, therefore originating the final formulation of the present work.

Table 3: test sensory parameters (0 to 5 scale).

TEST	A	B	C	D	E	F
T2	3	4	4	3	1	4
T2.2	3	5	3	3	1	5
T3.1	4	2	1	5	5	1
T3.2*	4	4	1	5	5	1
T4	4	0	0	2	3	1
T5	4	1	0	2	3	2
T6	3	5	0	2	3	5
T7.1	4	0	0	3	4	0
T7.2*	4	1	0	3	4	1
T8	4	0	0	3	3 – 4	0
T9	4	1	0	2	3	1
T10	4	0	5	3	5	0
T11	5	0	0	0 - 1	1	0
T12	5	0	0	0 - 1	1	0
T13	4	0	3	4	4	0
T14	4	0	2	4	4	0
T15	4	0	4	3	5	0
T16	4	0	4	3	5	0
T17.1	4	0	5	4	5	0
T17.2	4	0	5	5	5	0
T17.3	4	0	5	4	5	0
T17.4	4	0	5	4	5	0
T18.1	4	0	3	4	4	0
T18.2	4	0	2	5	4	0
T19	4	0	2	4	4	0
T20	4	0	1 - 2	4	4	0
T21	4	1	1 - 2	4	4	0
T22	4	0	1	4	4	0
T23	4	0	1	4	4	0
T24	4	0	2	5	4	0
T25	4	0	2	4	4	*
T26	3	1	2	4	4	2
T27	4	0	2	5	4	0
T28	2	1	2	4	5	2
T29	2	1	2	4	4	2
T30	2	1	2	4	4	2
T31	3	1	2	4	4	1
T32	4	2 – 3	2	4	4	1
T33	2	1	2	4	5	0
T34	2	1	1 - 2	4	5	0
T35	4	0	2	5	4	0
T36	3	1	1	4	5	1
T37	2 – 3	4	1	4	5	4
T38	3 – 4	1	2	5	5	0
T39	4	0	1 - 2	5	3	0
T40	0	na	na	na	na	na
T41	4	0	2	5	4	0

Table 4: Sensory parameters (0 to 10 scale).

TEST	A	B	C	D	E	F
T41	5	-	6	4	5	-
T42	3	+	6	na	2	+
T43	5	-	5	5	5	-
T44	5	-	5	5	5	-
T45	5	-	6	6	6	-
T46	5	-	7-8	6	7	-
T47	5	-	5	5	5	-
T48	5	-	6-7	5	5	-
T49	3	+	7-8	4	6	+
T50	3	+	7-8	4	6	+
T51	3	+	7	4	6	+
T52.1	5	-	5	5	5	-
T52.2	5	-	5-6	5	5	-
T53	5	-	6-7	5	5	-

+: presence
-: absense

Stability Tests

After the completion of the cycles of stability tests, the sample solidified again (after 24h) maintaining the rigidity characteristics of the solid emulsion, however its color was slightly lighter, as shown in Figure 1. The original aroma remained, but with less intensity. The pH changes a little from 4.68 ± 0.006 to 4.78 ± 0.05 but the density remained the same after all the stability tests, 0.73 kg / m3.

Figure 1: (a) sample after 6 cycles of accelerated stability tests; (b) control sample.

Identification of phenolic compounds from acorn by-products (Quercus ilex L.)

The qualitative results of the UHPLC-DAD-ESI-MS2 analysis of the polar extract of the acorn by-product (Quercus ilex) are illustrated in Figure 2, referring to the chromatogram obtained at 280 nm. Highlighting the majority compounds in the sample, Trigaloil-HHDP-glucose (peak 13), Valoneic acid dilactone (peaks 14) and gallic acid (peak 3).

Characterization of the after use of the moisturizing emulsion for the skin

Containing essential oils of mandarin, geranium, coriander and cinnamon seeds, which bring a touch of velvety freshness to the aroma, an aroma that proved to be the second point that most pleased the participants (47.6%) in a post survey use of "solid cream", second only to the hydration effect that receives 90.5% acceptance. The development and evaluation of the solid emulsion by a small sample of 21 individuals, revealed an excellent adherence and satisfaction to this product rich in fatty acids and special compounds, such as the extract of the acorn by-product

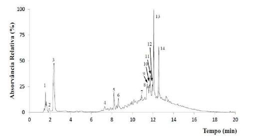

Figure 2: Chromatographic representation of the hydroalcoholic extract of the acorn by-product (Quercus ilex L.) at 280 nm. The numbers in the figure correspond to the UHPLC-DAD-ESI-MSn peaks.

Conclusion

During the development of this study, it was possible to verify in different ways the interactions of the emulsification process and the emulsifying and co-emulsifying agents in a cosmetic emulsion, especially when we change the proposal from consistency to solid.

Most of the emulsifiers available on the market are O / A type, when deciding to develop a solid emulsion the number of fats and lipophilic compounds increased and the search for an A / O emulsifier was necessary, however because it is also a biological cosmetic emulsion, subject to COSMOS certification, the number of emulsifiers available for testing are even more restrict, which made the development of the project challenging and engaging.

Water, whether pure or in the acorn extract itself, proved to be fundamental in the formulation, even though it is a solid emulsion, with a greater effectiveness of the emulsification process and a greater hydration effect, similar to the hydrating creams available on the market , where, for the most part, water is the main ingredient.

As for the tests of accelerated stability, the relative density of the solid emulsion remained at 0.73 Kg / cm3, there was no relevant pH variation, although the color of the sample has changed to a slightly lighter tone. As for the reduction of the intensity of the aroma, it was already foreseen, since the essential oils are thermosensitive compounds and, therefore, easily volatile with sudden temperature fluctuations.

Most of the sample participants who evaluated the solid moisturizing cream developed in this study, after using it, classify their skin as normal (42.90%) or dry (33.90%), which may justify the demand for more oils and greater adhesion to this solid emulsion rich in fatty acids.

The extract of the acorn by-product (Quercus ilex L.) revealed a great commercial potential for the cosmetic industry, especially biological, since it is a by-product and therefore, the reuse of a waste is essential in reducing the environmental impact, and to grow awareness for a deeper academic interest in the investigation and qualification of this by-product.

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References

[1] About the COSMOS Standard. https://www.cosmos-standard.org/about-the-cosmos-standard; Access at 2021, January 11.
[2] S. A. O. Santos, P. C. R. O Pinto, A. J. D Silvestre, C. P. Neto. Industrial Crops and Products 31 (2010) 521–525.
[3] M.A. Bonache, S. Moreno-Fernández, M. Miguel, B. Sabater-Muñoz, R. González-Muñiz. ACS Combinatorial Science 20 (2018) 694-699.
[4] C. F. S. Matos. Universidade Nova de Lisboa. (2019).
[5] https://cosmetics.specialchem.com/product/i-caroi-line-cosmetica-olive-squalane-wax. Acess date 2021/01/11.

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