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Micellar and Solvent Loan Chemical Extraction as a Tool for the Development of Natural Skin Care Cosmetics Containing Substances Isolated from Grapevine Buds

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Abstract: The present study aimed to evaluate the possibility of using micellar and solvent loan chemical extraction (LCE) to isolate valuable components from grapevine leaf buds, subsequently utilizing them to prepare functional and safe-to-use cosmetic preparations, specifically facial serums. An aqueous solution of polyglyceryl-4 laurate/sebacate and polyglyceryl-6 caprylate/caprate was employed for a micellar LCE, while an aqueous solution of 1,3-propanediol was used for a solvent LCE. Importantly, the extraction medium was exclusively comprised of components from the designed final cosmetic product. Consequently, no additional substances were present in the cosmetics developed, and the formulation was notably enhanced by compounds extracted from grapevine buds. The antioxidant properties and compound characterization of the obtained micellar (SurfE) and solvent (SolvE) extracts based on grapevine buds were tested and compared. UPLC-MS/MS results indicated that the extracts were rich in phenolic and flavonoid compounds, exhibiting antioxidant activity as measured using the DPPH and ABTS scavenging ability. The extracts were used to prepare model facial serums, which underwent evaluation based on fundamental functionality-related parameters (e.g., rheological characteristics and color) and their impact on the skin through cytotoxicity assessment. The results demonstrated that facial serums with extracts based on grapevine buds provided safe, natural cosmetics.

Keywords: loan chemical extraction; cosmetics; grapevine bud extracts

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1. Introduction

The historical utilization of plants in cosmetic formulations traces back to ancient times, a tradition that persists as a subject of contemporary scientific exploration. Over the years, advancements in our comprehension of both skin behavior and plant properties have contributed to increasingly intricate insights [1,2]. Plants, as complex organisms, intricately synthesize diverse metabolites in response to their environmental context. When applied to the skin, these phytomolecules engage with skin cells, exerting influences on the appearance and well-being of the skin. The amalgamation of ethnobotanical studies and physico-chemical analyses has unveiled a diverse inventory of plants, holding the potential to enhance modern cosmetic products with their unique attributes.

The fruits of plants, constituting the fundamental components of various plant species, are notable for their abundance of biologically active substances. These compounds,

concentrated in plant organs, find applications in food production, pharmacology, and cosmetics. Plants serve as important reservoirs of biologically active compounds [3,4]. The diverse compounds present in plants, including polyphenols, vitamins (A, B, C, and E), terpenes, and organic acids, have contributed to their widespread use in traditional medicine worldwide [5–8].

While fruits are prominent industrial products, leaves and their buds, with unique chemical compositions and excellent flavors, hold potential applications in herbal and cosmetic industries. Notably, blackcurrant buds are recognized for their anti-inflammatory properties and efficacy against skin conditions like eczema and psoriasis, while blackberry sprouts have found applications in traditional medicine due to their healing antioxidant, anti-hemorrhoidal, and anti-diarrheal properties [9–14].

The search for bioactive substances in alternative plant organs, such as young shoots or leaves, is becoming increasingly important. Scientific studies have confirmed the presence of health-promoting and antioxidant compounds in these parts of plants. It has been reported that young plant organs often contain higher concentrations of various bioactive compounds, positioning buds as potentially excellent reservoirs of these valuable substances [15–17].

Despite the long history of phytotherapy, recent years have seen its evolution into a well-established medical specialty. Scientific analysis has been applied to traditional knowledge to provide evidence of efficacy [18].

Notably, berries, such as the shoots of blackberries (cultivated varieties of Rubus) and the buds of blackcurrants (*Ribes nigrum* L.), stand out for their substantial content of vitamins, terpenic, and phenolic compounds, including phenolic acids, flavonols, and catechins [19,20]. In this context, preparations from buds, such as those derived from blackcurrant and blackberry, have attracted much attention [21,22]. The quality and efficacy of herbal medicines depend on various factors, including the genotype of the plant, pedoclimatic factors, agronomic procedures, phenological stage during harvest, and subsequent processing and storage procedures [23,24].

An essential consideration in contemporary practices is the dedicated commitment to environmental care. This commitment is exemplified through initiatives aligning with sustainable development principles [25] and, in some instances, the "zero waste" ideology [26]. Researchers, leveraging cutting-edge research methods and infrastructure, are increasingly directing their efforts towards harnessing production or agricultural waste as a source of intriguing and valuable raw materials [27]. These products, characterized by effectiveness, cost-efficiency, and bio-sustainability, emerge as noteworthy alternatives to conventional plant extracts commonly employed in the cosmetics industry. An example of this approach is the use of grape pomace derived from wine production [28,29]. Winery wastes, abundant in bioactive compounds, vitamins, edible acids, and dietary fibers, among others, offer a promising avenue for the production of value-added components [30,31] and are the object of many studies. Grapevine leaf buds are a material of relatively low popularity. Despite the enormous potential inherent in buds, their use remains relatively unpopular, overshadowed by the well-established popularity of their fully developed counterparts—edible fruits renowned for their rich nutrient content.

Various extraction methodologies can be employed to isolate and fractionate valuable substances from plant material. While different extraction technologies are available, steam/water distillation and extraction via organic solvents, together with their respective modifications, have remained prominent as the primary industrial processes for obtaining volatile and non-volatile fractions, respectively [32–38].

This article introduces a novel approach to cosmetic manufacturing, emphasizing the crucial role of "loan chemical extraction" (LCE), a distinctive method characterized by an extraction process involving ingredients borrowed from the final cosmetic product [39]. The extraction medium is an aqueous solution containing the compounds that constitute the ingredients of the cosmetic being produced. In contrast to conventional practices, where extracts are typically introduced during the main stages of cosmetic mass production, LCE

redefines the production process by incorporating the extraction step as an integral part of cosmetic manufacturing.

In our earlier investigation, we explored the extracts derived through the LCE from grape pomace, a by-product of wine production. The formulation of the extraction medium was carefully selected from the designed final cosmetic product to generate aggregates (micelles) within the bulk phase. This targeted composition facilitated the efficient leaching of cosmetically valuable bioactive components from the plant material, following the principles observed in micellar extraction [40,41].

In this work, the effectiveness of two extraction media, both prepared exclusively from ingredients contained in the formulation of the cosmetic under development, was compared. The first medium involved micellar extraction with aggregates (micelles) obtained in the bulk phase. The second medium utilized traditional solvent extraction, employing a natural, plant-delivered solvent. The focus is on demonstrating the feasibility of incorporating LCE into the production of personal care cosmetics. Grapevine buds are used as the plant material for this innovative extraction method.

The starting material for the study was waste shoots cut from the vine bushes during the winter period. The shoots were then induced to produce leaf buds under controlled laboratory conditions. In a further step, the buds were mechanically removed once they had reached an appropriate size. The plant material thus prepared was subjected to the LCE process. The obtained extracts were characterized to elucidate the profile and activity of bioactive compounds isolated from young buds through LCE. Subsequently, these extracts were formulated into a model skincare cosmetic, particularly facial serums. The study entailed the development and preparation of a model of natural skincare cosmetics, with empirical verification of their functionality and safety parameters. This innovative approach represents a significant step forward in the evolution of cosmetic manufacturing, emphasizing the potential of LCE in creating natural and effective skincare products.

2. Materials and Methods

2.1. Chemicals and Reagents

Analytical standards for ferulic and vanillic acids, rutin, D-(−)-quinic acid, apigenin, (+)-catechin, (−)-epicatechin 3-gallate, and antibiotics (1000 µg/mL streptomycin and 100 U/mL penicillin), Dulbecco's modification of Eagle's medium (DMEM), and phosphate-buffered saline were provided by Merck (Darmstadt, Germany). Gallic acid, quercetin, ABTS, and Trolox were sourced from POL-AURA (Zabrze, Poland), while trans-resveratrol was obtained from LGC (Teddington, Middlesex, the UK). The DPPH, acetic acid, neutral red solution, resazurin sodium salt, and trypsin-EDTA solution were acquired from Sigma Aldrich (Saint Louis, MO, USA). All utilized standards were of analytical grade (≥99%). ACN and MeOH of LC-MS grade were supplied by J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water was purchased from the Direct-Q water purification system.

The facial serums were developed based on certified, plant-delivered raw materials approved by COSMOS and ECOCERT standards for the production of natural products:: polyglyceryl-4 laurate/sebacate (and) polyglyceryl-6 caprylate/caprate (Natragem S140, Croda, Krakow, Poland), 1,3-propanediol (Cosphaderm, propanediol natural, BASF, Ludwigshafen, Germany), benzyl alcohol, benzoic acid, dehydroacetic acid, tocopherol (Schülke and Mayr GmbH, Norderstedt, Germany), and lactic acid (Krakchemia, Krakow, Poland).

2.2. Plant Material

The plant's raw material—woody shoots—was obtained from the annual cutting of grapes grown at the Estro Vineyard (Ujazd, Poland). On 8 December 2021, shoots of red grapes of the hybrid variety Léon Millot (Millardet et Grasser 101 O.P. × *Goldriesling* × *Vitis rupestris* × *Vitis riparia*) were collected.

The shoots were cut to a proper length of approx. 30 cm. The bottom of the shoots was scraped off from the outer layer of the cortex down to the level of the vital tissue and cut perpendicular to the shoot. The tops of the shoots have been treated with a gardening

ointment with fungicidal properties. Such prepared shoots were placed in a styrofoam incubator with the perlite on 9 December 2021 under laboratory conditions. The dimensions of the incubator were as follows: 40 × 40 × 50 cm with a wall thickness of 5 cm. The base of the incubator was equipped with an electric heater with a temperature regulator to maintain a temperature range between 26 and 28 °C and filled with perlite to a height of approx. 20 cm before the shoots were placed in it. Throughout the rooting period, the temperature was kept at around 26 and 28 °C with daily watering and irrigation of the shoots (Estro vineyard's own methodology of reproducing juvenile grape cuttings from shoots).

The first buds appeared on 10 January 2022, and the last collection was performed on 3 February 2022. A total of 86 g of buds were obtained.

2.3. Micellar-Extraction medium Characterization

Critical Micellar Concentration (CMC)

The critical micellar concentration (CMC) was determined at 25 °C using the tensiometry method. A tensiometer equipped with a platinum ring (Krüss K9-Mk1, Hamburg, Germany) was applied to measure the surface tension at varying surfactant concentrations [39,42]. The surface tension values were measured in triplicate.

2.4. Solvent and Micellar LCE of Grapevine Buds

Prior to performing the LCE process of grapevine buds, the solvent and micellar extraction media were prepared. A 4 wt. % aqueous solution of the polyglyceryl-4 laurate/sebacate and polyglyceryl-6 caprylate/caprate surfactant mixture (compound borrowed from a final facial serum composition) was used as the micellar-extraction medium. For the solvent-extraction medium, an aqueous solution of 1,3-propanediol at the concentration of 4 wt. % was utilized.

Harvested, deep-frozen grapevine buds were ground in a laboratory knife mill (Cutter Mixer R5 Plus, Robot Coupe, Palinges, France) with the addition of dry ice.

A total of 15 g of ground grapevine buds were dispersed in 150 g of the micellar-extraction medium and automatically shaken for 3 h at room temperature, at 2500 rpm (BenchMixer XL multi-tube vortexer, Benchmark Scientific, Sayreville, NJ, USA), yielding the micellar extract (Surf E). Similarly, the solvent extract (SolvE) was obtained by dispersing 15 g of ground grapevine buds in 150 g of a solvent-extraction medium. Table 1 displays the formulation used to prepare the micellar and solvent extracts.

Table 1. Ingredients and their concentrations used to prepare the micellar and solvent extracts.

	Ingredient (INCI Name)	SurfE [wt. %]	SolvE [wt. %]
1	polyglyceryl-4 laurate/sebacate (and) polyglyceryl-6 caprylate/caprate	4	-
	1,3-propanediol	-	4
2	benzyl alcohol, benzoic acid, dehydroacetic acid, tocopherol	0.5	0.5
3	aqua	85.5	85.5
4	grapevine buds	10	10

The prepared solvent and micellar extracts were vacuum filtered (Vacuum Pump V-700, Büchi, Flawil, Switzerland). A non-woven polyester (ULESTER 32S) and polyamide (UHELON 53S) filters (Silk and Progress, Brněnec, Czech Republic) were used. The filtrates underwent centrifugation for 10 min at 7500 rpm (Universal 320R centrifuge, Andreas Hettich GmBH, and Co, Tuttlingen, Germany). Then, a 0.5% mixture of benzyl alcohol, benzoic acid, dehydroacetic acid, and tocopherol was added to the resulting solutions as a preservative. The solvent and micellar extracts of grapevine buds prepared this way were used directly in the following studies.

2.5. Determination of Bioactive Compounds

Quantitative Analysis of Selected Compounds in Grapevine Bud Extracts Using Ultraperformance Liquid Chromatography Coupled with Tandem Mass Spectrometry (UPLC-MS/MS)

The investigation of specific compounds in grapevine bud extracts was carried out employing a methanol dilution. The resulting solutions were separated using a liquid chromatograph (Sciex ExionLC AD, AB Sciex, Concord, ON, Canada) with a reverse-phase column (Kinetex 3.5 µm XB-C18 100 Å; 100 × 4.6 mm, Phenomenex, Torrance, CA, USA). The separation of compounds was accomplished using gradient elution, with the specific details outlined in a previous publication [24]. The tandem mass spectrometer (MS/MS) (QTRAP 4500, AB Sciex, Concord, ON, Canada) with an electrospray ionization (ESI) was working in positive and negative modes. The ionization source was configured with specific parameters, wherein the ion spray voltage was established at 4500 V in positive-ion mode and −4500 V in negative-ion mode. The source temperature was maintained at 650 °C. Nebulizing, drying, and curtain gas pressure were set at 50 psi, 50 psi, and 35 psi, respectively. The Analyst version 1.7.2 was used for data analysis. For the quantification of SurfE and SolvE, the multiple reaction monitoring (MRM) scan mode was employed. The MS/MS parameters characteristic for specific compounds are summarized in Table S1.

The peak areas of the most intense MRM transition were used to plot a nine-point calibration curve for each standard in the range from 0.2 to 40 µg/mL. In contrast, catechin concentration ranges from 0.02 to 2.5 µg/mL. Vine bud extracts were dissolved in methanol at a ratio of 1:9 (v/v), filtrated using 0.2 µm syringe filters, and analyzed using LC-MS/MS.

2.6. Determination of Antioxidant Properties

2.6.1. Total Phenolics Content (TPC)

The assay of TPC for the grapevine bud extract was conducted using the Folin–Ciocalteu (FC) method [43] with slight modification. In this approach, 20 µL of the grapevine buds extract, and 20 µL of distilled water were combined with 200 µL of the FC reagent and 600 µL of a 20% sodium carbonate solution. Subsequently, the solutions were adjusted to a final volume of 4 mL with distilled water and incubated without light exposure for 2 h before measuring their absorbance at 765 nm (HP-Hewlett Packard, model: 8452A, Palo Alto, CA, USA).

2.6.2. Total Flavonoid Content (TFC)

TFC determination in the grapevine bud extract was performed following a modified version of the method initially outlined by Chang et al. [44]. In this adapted procedure, 300 µL of the grapevine bud extract was mixed with 700 µL of methanol, 60 µL of 10% aluminum chloride, and 60 µL of 1 M sodium acetate. The resulting solutions were diluted with distilled water to a final volume of 4 mL and incubated at room temperature for 30 min. Subsequently, the absorbance was measured at 420 nm. All analyses were conducted in triplicate.

2.6.3. Antioxidant Activity (DPPH Test)

The antioxidant activity of the grapevine bud extract using the DPPH radical assay was evaluated following the method described by Brand-Williams et al. [45]. Initially, 30 µL of the grapevine bud extract was combined with 970 µL of methanol, and the resultant solution was mixed with 3 mL of a 0.1 mM DPPH methanolic solution. The resulting mixture was thoroughly shaken and allowed to stand without exposure to light for 30 min. Subsequently, the absorbance was measured at 517 nm against the blank (methanol). All determinations were carried out in triplicate.

2.6.4. Antioxidant Activity (ABTS Test)

The antioxidant activity of the grapevine bud extract using the ABTS test was determined using a modified method described by Re et al. [46]. The ABTS+ radical solution was prepared by reacting 1 mL of 0.01 M ABTS with 1 mL of 0.005 M potassium persulfate.

The resulting mixture was kept for 20 h without exposure to light. Subsequently, 30 µL of the grapevine bud extract and 970 µL of distilled water were mixed with 2 mL of the ABTS+ solution. The absorbance was read after 6 min, at 734 nm, against water as a blank. The determinations were performed in triplicate.

The percentage of the DPPH and ABTS scavenging effect was calculated using the formula:

$$\% \text{ Scavenging} = [(\text{Acontrol} - \text{Asample})/\text{Acontrol}] \times 100 \quad (1)$$

where Asample is the absorption of the solution containing the extract, and Acontrol signifies the absorbance of the solution without the extract.

2.7. Color Parameters Determination of the Grapevine Bud extracts

Solvent and surfactant extracts from grapevine buds underwent color reflectance measurements using CM-3600 Konica Minolta (Sensing Singapore Pte Ltd., Tokyo, Japan). Data evaluation was performed using CM-S100w SpectraMagic NX, ver. 1.07 data color software. The determination of color parameters was performed using the CIE LAB system, which employs a three-dimensional color space defined in L*, a*, and b* rectangular coordinates [39]. Briefly, the L* axis signifies color lightness, with 0 for black and 100 for white. Axes a* and b* correspond to variations in red–green and yellow–blue, respectively (+a* for red, −a* for green, +b* for yellow, and −b* for blue). Chromaticity coordinates (a* and b*) are characterized in polar coordinates through chroma (C*) and the hue angle (h^o), as stated by Equation (2) and Equation (3), respectively.

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (2)$$

$$h^o = \arctan\frac{b^*}{a^*} \quad (3)$$

2.8. Model Facial Serum Preparation

Model skincare cosmetics, specifically facial serum (FS), were designed and prepared. All the ingredients utilized complied with EcoCert and COSMOS requirements. The compounds used for formulation, along with their weight percentages, are presented in Table 2.

Table 2. Composition of designed model cosmetics (facial serum).

		FS_Solv Facial Serum Based on Solvent without Extract	**FS_SolvE Facial Serum Based on Solvent with Extract**	**FS_Surf Facial Serum Based on Surfactants without Extract**	**FS_SurfE Facial Serum Based on Surfactants with Extract**
	Ingredient (INCI Name)	**[wt. %]**	**[wt. %]**	**[wt. %]**	**[wt. %]**
1	aqua	60	60	60	60
2	xanthan gum	0.6	0.6	0.6	0.6
3	benzyl alcohol, benzoic acid, dehydroacetic acid, tocopherol	0.5	0.45	0.5	0.45
4	sodium hydroxide/lactic acid	to pH 5.5	to pH 5.5	to pH 5.5	to pH 5.5
5	polyglyceryl-4 laurate/sebacate (and) polyglyceryl-6 caprylate/caprate	-	-	0.4	-
6	propanediol	0.4	-	-	-
7	extract with surfactant	-	-	-	10.0
8	extract with solvent	-	10.0	-	-
9	aqua	to 100	to 100	to 100	to 100

The preparation of model facial serums followed a carefully planned procedure, with all operations conducted at room temperature. In the initial step, xanthan gum was dispersed in a portion of water, ensuring thorough mixing while taking precautions to prevent the introduction of air into the system. Simultaneously, the remaining portion of water was placed in a separate container.

For the preparation of FS_Surf or FS_Solv, polyglyceryl-4 laurate/sebacate (and) polyglyceryl-6 caprylate/caprylate or 1,3-propanediol, respectively, was added to this water, along with a mixture of benzyl alcohol, benzoic acid, dehydroacetic acid, and tocopherol as a preservative.

In the case of the preparation of FS_SurfE and FS_SolvE, an appropriately designed grapevine bud extract was added in the amount of 10% of the stock solution instead of part of the water, and then, the missing preservative concentration was completed.

2.9. Assessment of the Cytotoxicity of the Tested Facial Serums on Keratinocytes

2.9.1. Cell Culture

The cytotoxicity assessment of the developed facial serums was performed on human HaCaT keratinocytes (CLS Cell Lines Service, 300493, GmbH, Eppelheim, Germany). These cells were cultured in Dulbecco's Modified Essential Medium (DMEM) with L-glutamine and the addition of 10% (*v*/*v*) FBS (fetal bovine serum). Antibiotics were used to protect cells against microbial infection (100 U/mL penicillin and 1000 µg/mL streptomycin). The cell culture was conducted at 37 °C in an incubator under a humidified atmosphere containing 95% air and 5% carbon dioxide (CO_2). When the cells reached the appropriate confluence (around 70–80%), they were transferred to 96-well plates at a density of 1×10^4 cells per well and exposed to the test samples.

2.9.2. Alamar Blue Assay (AB)

To evaluate the metabolic activity of HaCaT cells after treatment with the tested facial serums (FS_Solv, FS_SolvE, FS_Surf, and FS_SurfE), the AB test was used, following the procedure described by Page et al. with modifications [47]. Keratinocytes were incubated at concentrations of 0.01%, 0.1%, and 1.0% (*v*/*v*) in a DMEM medium for 24 h. Subsequently, the sample medium was aspirated, and a 60 µM of resazurin solution (Merck KGaA, Darmstadt, Germany) was added to each well. Control cells cultured in DMEM without the addition of test samples were used as a reference. The plates were then incubated for 2 h, and fluorescence at λ = 570 nm was measured using a FilterMax F5 microplate reader (Thermo Fisher Scientific, Waltham, MA, USA). The analyses were conducted in three independent experiments, with each sample tested in four replicates.

2.9.3. Neutral Red Assay (NR)

To assess the viability of HaCaT cells in contact with the tested facial serums, an NR uptake assay was used according to the methodology reported by Borrenfreund et al. using slight modifications [48]. Keratinocytes were incubated with the tested facial serums at concentrations of 0.01, 0.1, and 1.0% (*v*/*v*) for 24 h. Afterward, the sample culture medium was aspirated, and NR dye (at a concentration of 40 µg/mL) was applied to each well of a 96-well plate. The test samples were incubated for 2 h at 37 °C. The NR dye was then removed, and the cells were washed twice with sterile PBS. Subsequently, PBS was aspirated from the wells, and 150 µL of a methanol/acetic acid/water (50%/1%/49%) as a decolorization solution was added. Absorbance at λ = 540 nm was directly measured with the FilterMax F5 microplate reader (Thermo Fisher Scientific, Waltham, MA, USA). Analyses were conducted in three independent experiments, with each sample measured in four replicates.

2.10. Rheological Behavior

The rheological behavior of the designed facial serum was characterized via rheograms obtained using the viscosity assay at different share rates using the DV2TRV Brookfield

rheometer (Brookfield, WI, USA) [39]. A total of 8 mL of the cosmetics sample was filled into a small sample adapter with a controlled temperature. The SC4 spindle with a cylindrical shape was used for facial serum viscosity analysis. The measurement was performed at 20 °C in triplicate.

2.11. Microbiological Stability

The microbiological stability of the grapevine bud extracts and facial serum was determined using microcount® duo microbiological testers (Schülke and Mayr GmbH, Norderstedt, Germany). The test slides were immersed into a tested extract and facial serums for approximately 10 s. Microbiological plates were placed in the tester vial and stored in the incubator at 28 °C (KPK60, mytron Bio- und Solartechnik GmbH, Heilbad Heiligenstadt, Germany) for 3 days to evaluate fungi and bacterial colonies, and for 5 days to examine yeast and mold, respectively. After the indicated time, the number of microorganisms was quantified by visually evaluating the plates using the template provided by the manufacturer.

2.12. Chemical Stability

The mechanical loading test was used to evaluate the chemical stability of the designed facial serums. After 24 h from the preparation of serum samples, the resulting cosmetics were subjected at room temperature to a centrifugal force of 3000 rotations per minute for 30 min.

2.13. Statistical Analysis

All data were presented as mean ± standard deviation (SD), with three replications for each sample (n = 3) in the case of UPLC-ESI-MS/MS and six replications for color parameter determination (n = 6). The antioxidant properties assay was conducted in triplicate. Cytotoxicity analyses were carried out in three independent experiments, each comprising four replicates per treatment group. Mean values were compared using ANOVA and a Tukey's honestly significant difference (HSD) post hoc test, and differences were considered significant when the p-value was <0.05. Calculations were performed using the software package Statistica ver. 10 (StatSoft, Tulsa, OK, USA).

3. Results

3.1. Development of Micellar and Solvent Loan Chemical Extraction for Obtaining Cosmetically Valuable Compounds from Grapevine Buds

In this work, LCE was used to prepare grapevine bud extracts for model facial serums. Developing an effective extraction medium with ingredients mirroring those intended for the final product was a fundamental objective of this study. Two final cosmetic compositions were developed either based on surfactants or on the organic solvent solution. A surfactant mixture, specifically polyglyceryl-4 laurate/sebacate and polyglyceryl-6 caprylate/caprate, was chosen for its ability to form micelles—associative aggregates in aqueous solutions. The formation of micelles provides a favorable environment in the bulk phase wherein hydrophobic substances can be effectively solubilized. Consequently, this type of system was employed in the micellar extraction process to isolate bioactive compounds from grapevine buds.

A mixture of polyglyceryl-4 laurate/sebacate and polyglyceryl-6 caprylate/caprate is a naturally derived solubilizer known for facilitating the incorporation of a broad range of lipophilic ingredients into clear formulations. In this study, a concentration of 4% wt. % of this surfactant was employed to prepare the micellar-extraction medium. In order to confirm the presence of micelles in solution at the concentration used, surface tension measurements were carried out at different concentrations of the surfactant system to determine the CMC value. As shown in Figure 1, the surface tension of the surfactant mixture decreased with an increasing concentration expressed on a logarithmic scale. When the critical concentration was reached, the surface tension achieved a plateau, indicating

that micelles were formed. The CMC value for the polyglyceryl-4 laurate/sebacate and polyglyceryl-6 caprylate/caprate mixture was determined from the inflection point on the plot of surface tension versus the logarithm of concentration. According to the obtained results, it was found that micellization occurred at a surfactant concentration of 0.012 wt. %. It is important to note that the surfactant concentration of 4 wt. % used in the extraction medium for LCE significantly exceeded the CMC by more than 300 times.

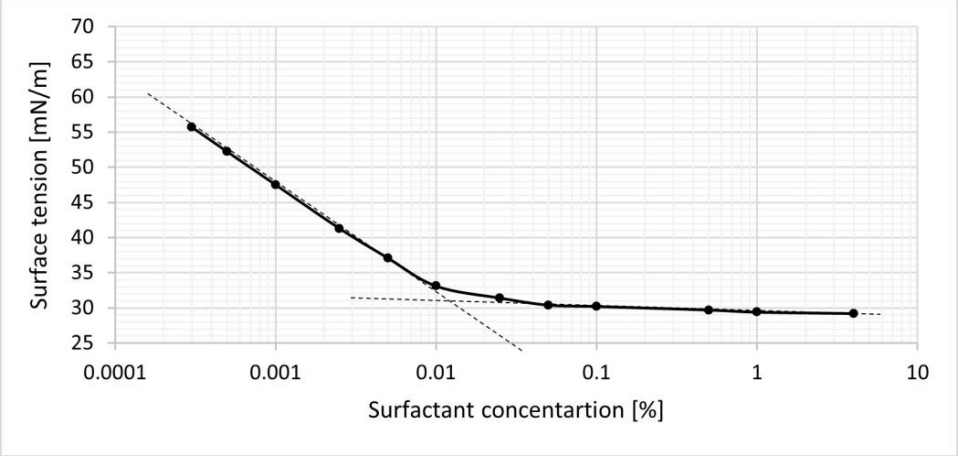


Figure 1. Plot of change in surface tension relative to surfactant concentration for CMC assessment. The point of intersection of the dashed lines is indicated by the CMC value.

This careful consideration of surfactant concentration and micelle formation ensures the efficacy of the extraction process, confirming the suitability of the chosen surfactant system for the micellar-extraction medium. The significant exceedance of CMC via the selected surfactant concentration suggests that the threshold required for effective micelle formation is achieved, thus further emphasizing the effectiveness of the selected extraction medium in solubilizing lipophilic components from the plant material.

For comparison, naturally derived 1,3-propanediol was used for the solvent LCE process. The 1,3-propanediol was chosen as an environmentally sustainable and skin-friendly compound.

Within a controlled laboratory setting, grapevine buds were obtained and subjected to extraction. The plant material under investigation is presented in Figure 2.

The milled and powdered grapevine buds were dispersed in either a micellar or solvent-extraction medium resulting in the generation of SurfE and SolvE extracts, respectively.

These extracts were subjected to comprehensive characterization to unveil the profile and activity of bioactive compounds isolated from young buds through the LCE process. Subsequently, the extracts were incorporated into a model skincare cosmetic specifically designed as facial serums.

This research involves the development and formulation of model natural skincare cosmetics, including the empirical verification of their functionality and skin safety parameters. The proposed innovative approach represents a significant advance in the landscape of cosmetic manufacturing, highlighting the potential of LCE and grapevine buds in the development of natural and effective skincare products.

Figure 2. The grapevine buds used for studies.

3.2. Determination of Selected Compounds via UPLC-MS/MS

Waste materials from winemaking, such as grape buds, possess potential associated with polyphenolic compounds. This suggests their secondary utilization, emphasizing their contribution to sustainable practices in the grapevine industry [49].

To evaluate the quantity of selected polyphenolic compounds in grapevine buds extracted using two different ways, UPLC-MS/MS was employed. The extracted ion chromatograms (XIC) obtained for selected compounds in SurfE and SolvE in negative ionization mode are presented in Figures S1 and S2, respectively, in Supplementary Materials, and the calculated data are presented in Table 3.

To assess their collective contribution to the phytochemical composition of grapevine bud polyphenols, the study analyzed health-promoting components from six classes of phenolic compounds: flavonols (rutin and quercetin), phenolic acids (gallic acid and vanillic), flavanols ((+)-catechin and (−)-epicatechin 3-gallate), cinnamic acids (*trans*-ferulic acid), flavonones (apigenin), and stilbenes (*trans*-resveratrol).

The primary phenolic compounds in both micellar and solvent extracts were quinic acid (78.8 mg/kg and 54.5 mg/kg, respectively) and gallic acid (10.8 mg/kg and 9.0 mg/L, respectively). Moreover, extracts from buds obtained through micellar extraction exhibited a higher content of both of these antioxidants. The literature emphasizes the potential antibacterial, antiviral, and antifungal properties of quinic acid [50].

Table 3. Concentration of selected polyphenols isolated from buds expressed in mg of compound per kg of wet plant tissue (mg/kg WW). Different superscript letters for each extract highlight the significant differences at $p < 0.05$.

Compound	SurfE	SolvE
Quinic acid	78.8 ± 0.8 [a]	54.5 ± 0.6 [b]
Gallic acid	10.8 ± 0.4 [a]	9.0 ± 0.4 [b]
Rutin	8.43 ± 0.28 [a]	3.43 ± 0.41 [b]
Apigenin	4.91 ± 0.05 [a]	5.07 ± 0.06 [a]
Vanillic acid	1.09 ± 0.06 [a]	1.08 ± 0.15 [a]
trans-Resveratrol	1.67 ± 0.09 [a]	1.65 ± 08 [a]
(−)-Epicatechin 3-gallate	1.07 ± 0.07	nd
Quercetin	0.46 ± 0.09	nd
(+)-Catechin	0.31 ± 0.02	nd
trans-Ferulic acid	0.35 ± 0.01	nd
Sum of polyphenols	107.9	74.8

As a result of the surfactant-assisted extraction of grapevine buds, 2.5 times more rutin is released compared to solvent extraction. Furthermore, the rutin content in SurfE from grape buds is almost five times higher than extracts obtained through LCE from grape pomace [39].

Apigenin, vanillic acid, and trans-resveratrol content were detected in both types of analyzed grapevine bud extracts but did not differ in amount in a statistically significant way (4.91 mg/kg, 1.09 mg/kg, and 1.67 mg/kg for SurfE and 5.07 mg/kg, 1.08 mg/kg, and 1.65 mg/kg for SolvE, respectively). Both catechins, quercetin and trans ferulic acid, were noted only in micellar extracts. Catechins have demonstrated positive effects in humans owing to their antimicrobial, anti-inflammatory, antioxidant, antiviral, antiallergenic, and anticancer properties. They enhance the penetration and absorption of skincare products into the body and skin, thereby enhancing their efficacy as well [51]. The utilization of catechin-rich preparations may play a beneficial role in inhibiting the proliferation of human cancer cells [52].

The data identified the analyzed grapevine bud extracts as an excellent source of polyphenols. The contribution of each class of polyphenols to the phenolic content is shown in Figure 3. UPLC-MS/MS analysis revealed that the quality profiles of polyphenolic compounds in both types of extracts were similar. However, using a surfactant resulted in a greater extraction of the phytocomplex compared to solvent isolation.

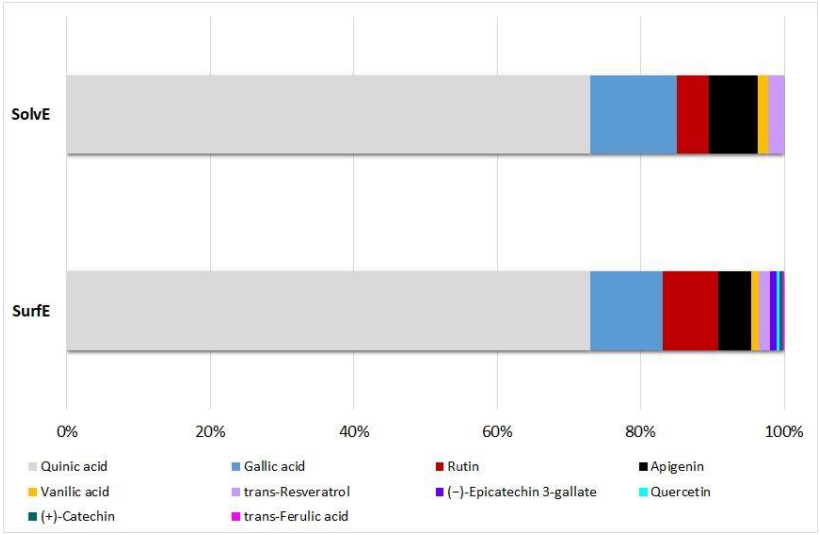


Figure 3. Phenolic compound composition profile for solvent (SolvE) and micellar (SurfE) grapevine bud extracts.

This study may confirm the potential use of grapevine bud products in skincare cosmetics. In addition, the beneficial effects of polyphenolic extracts in cosmetics contribute to improved skin health and appearance.

3.3. Total Phenolic, Flavonoids Content, and Antioxidant Activity (DPPH and ABTS)

According to the results presented in Table 4, it can be seen that the extraction method employed for sample preparation significantly influences the levels of total phenols, flavonoids, and antioxidant potential. Across all conducted tests, the outcomes consistently indicated markedly higher values for grapevine bud extracts when utilizing the micellar extraction method compared to solvent extraction.

Table 4. Total phenolic and flavonoid content along with antioxidant capacity (DPPH and ABTS) in grapevine bud extracts.

Grapevine Buds Extract	TPC [mg GAE/L]	TFC [mg QE/L]	DPPH [%]	ABTS [%]
SurfE	722 ± 13	57.6 ± 1.1	69.8 ± 1.7	42.4 ± 1.9
SolvE	486 ± 10	32.6 ± 0.7	60.1 ± 2.5	34.6 ± 1.4

The data represent the average obtained from three parallel measurements, and the results are expressed as mean ± SD.

Micellar extraction from buds resulted in higher yields of total phenolic and flavonoid content compared to solvent extraction. Specifically, SurfE extracts exhibited more than a 30% increase in phenolic content (722 ± 13 mgGAE/L) compared to SolvE extracts (486 ± 10 mgGAE/L). Similarly, for flavonoid (TF) content, SurfE demonstrated a 40% higher concentration (57.6 ± 1.1 mgQE/L) compared to SolvE (32.6 ± 0.7 mgQE/L). The antioxidant activity test results underscore the crucial role of the extraction method in obtaining bioactive compounds. Micellar extraction of grapevine buds produced an extract with approximately 10% stronger antioxidant activity compared to solvent extraction. Specifically, the SurfE bud extract exhibited significantly higher antioxidant activity (DPPH: 69.8 ± 1.7%, ABTS: 42.4 ± 1.9%) than the SolvE bud extract (DPPH: 60.1 ± 2.5%, ABTS: 34.6 ± 1.4%).

3.4. Determination of the Color Parameters of Grapevine Bud Extracts

To assess the color difference between the tested micellar and solvent grapevine bud extracts, colorimetric tests were conducted. Although both tested extracts showed a green-yellow hue (Figure 4), a comparison of the L*, a*, and b* values revealed differences in the color parameters of the obtained extracts (Table 5).

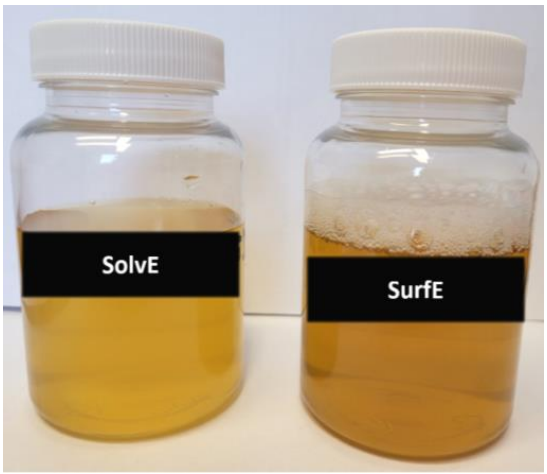


Figure 4. Color comparison of SolvE and SurfE.

Table 5. Spectrophotometric data of the grapevine bud extracts. Values are means of six replicate determinations ± standard deviation (n = 6). Different superscript letters for each extract highlight the significant differences at $p < 0.05$.

	L*	a*	b*	C*	h°	Color
SolvE	53.65 ± 0.04 [a]	−7.40 ± 0.01 [a]	19.29 ± 0.03 [b]	20.66 ± 0.03 [b]	111.00 ± 0.04 [b]	more greener yellow
SurfE	45.06 ± 0.02 [b]	−7.18 ± 0.01 [b]	29.52 ± 0.01 [a]	30.38 ± 0.01 [a]	103.66 ± 0.01 [a]	less greener yellow

SolvE exhibited greater lightness compared to SurfE. The use of micellar extraction resulted in the isolation of the grapevine bud components with a significantly more yellowish hue compared to the solvent extract. Simultaneously, while maintaining a similar negative value of the a* parameter suggesting a weak green tint for both extracts, the chroma (C*) value for SurfE is higher, visually perceived as a greater saturation compared to SolvE. The color shade is indicated by the hue angle (h°) values, allowing for an intuitive expression of the extract's color. It can be observed that SurfE has a greener yellow hue compared to SolvE, which is more yellow.

3.5. Application Analysis

Model cosmetics (facial serum, FS) were prepared, and their properties were investigated. The development of the model facial serums was guided by the goal of formulating safe-to-use cosmetic products with beneficial properties derived from bioactive components extracted from grapevine buds through LCE. The model cosmetic products underwent further testing to ensure they met the desired skin care performance.

3.5.1. Cytotoxicity Assessment

To evaluate the potential effect of the tested serums on skin cells, in vitro cytotoxicity analyses were performed on human keratinocytes (HaCaT). For this purpose, the Alamar blue and neutral red assays were used, which allowed for the assessment of metabolic activity and damage to cell membranes of cells treated with the tested samples. The analyses performed showed that none of the tested samples had a cytotoxic effect on keratinocytes in the tested concentration range (0.01–1.0%). Additionally, it was indicated that the addition of the grapevine bud extract to the formula of the analyzed serums (both in the case of surfactant and solvent extraction) may have a positive effect on the viability of these cells (Figures 5 and 6). The cytoprotective effect of the tested grapevine bud extract was observed in both cytotoxicity tests, which indicates both a positive effect on metabolic activity, resulting in the reduction in resazurin and the possibility of retaining neutral red in cell lysosomes. The positive effect of the tested extract on keratinocytes is probably the result of the presence of biologically active compounds such as gallic acid, rutin, quinic acid, ECGC, quercetin, or trans-reveratrol, which are phytochemicals with proven cytoprotective properties [53–56]. This effect, in addition to the ability to increase metabolic activity and maintain the proper structure and function of cell membranes, is probably related to the ability of grape extracts to enhance antioxidant protection and inhibit mediators of inflammation and oxidative stress [57,58]. Thus, this work demonstrated that the developed cosmetic preparations containing the obtained extract do not cause cytotoxic effects on keratinocytes in vitro, and this extract is able to limit the cytotoxic effects of both the solvent and the surfactant used.

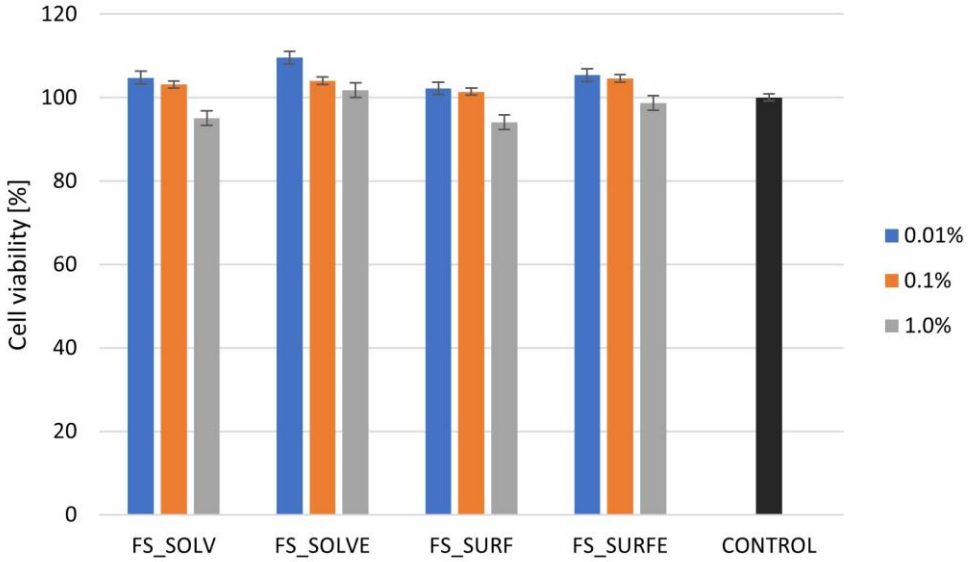


Figure 5. Assessment of resazurin reduction via keratinocytes (HaCaT) after a 24 h exposure to the tested facial serums (at concentrations of 0.01, 0.1, and 1.0%). The black bar shows control cells (not treated with the tested preparations) for which the viability was assumed to be 100%. Data are the mean ± SD of three independent experiments, each consisting of four replicates per treatment group.

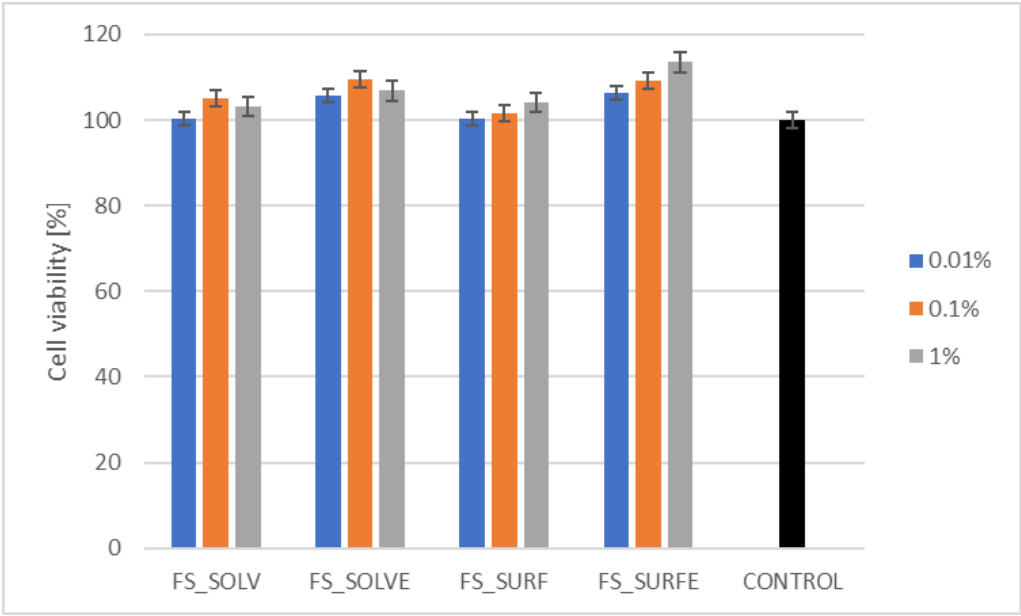


Figure 6. Assessment of the uptake of neutral red dye via keratinocytes (HaCaT) after 24 h exposure to the tested facial serums (at concentrations of 0.01, 0.1, and 1.0%). The black bar shows control cells (not treated with the tested preparations) for which the viability was assumed to be 100%. Data are the mean ± SD of three independent experiments, each consisting of four replicates per treatment group.

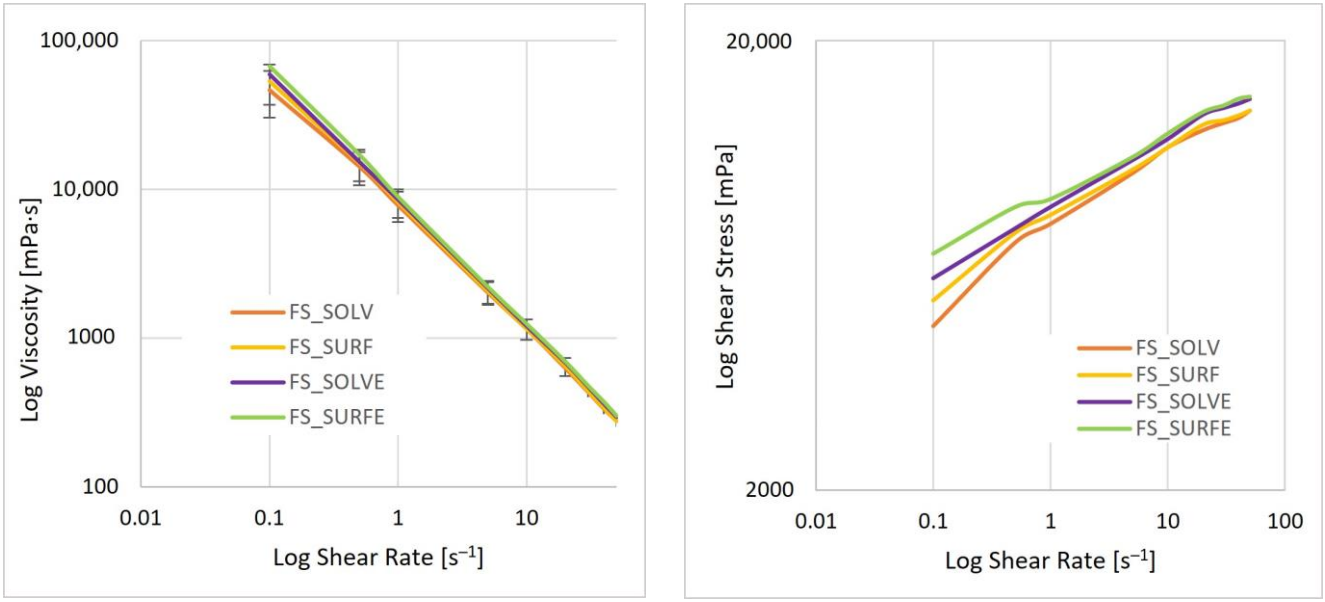
3.5.2. Rheological Behavior

In the field of cosmetic science, viscosity management is of paramount importance, having a profound impact on the overall perceived quality of the product as it determines its consistency and spreadability on the skin [59,60]. This significance is particularly evident in surfactant-based cosmetic systems, where precise viscosity control is a routine and crucial practice in industrial settings. This control relies primarily on the use of rheology modifiers to fine-tune the product's consistency. Achieving a certain viscosity level is not just a technical requirement but a fundamental necessity to ensure optimal dispensing of

the product from the package and to facilitate even spreading on the skin. Moreover, in cosmetic preparations, high relative viscosity is perceived among users as corresponding to high concentrations of active ingredients and high efficacy.

Rheological properties are often selected to align with the type of cosmetic product and its impact on the skin. Cosmetics designed for skin regeneration and irritation relief, especially those intended for dry and flaky skin, should linger on the skin's surface for an extended period [60–62], and these are commonly provided as creams and serums [63]. In this context, rheological modifiers play a pivotal role in adjusting the viscosity profile to meet desired specifications, thereby enhancing the consumer's experience with the product.

The rheological characteristics of the model facial serums obtained are visually represented in Figure 7. This analytical representation aids in comprehending the flow and deformation properties of facial serums, elucidating their practical suitability and consumer perceptions.



(**a**) (**b**)

Figure 7. Rheogram of model facial serums: (**a**) log viscosity vs. log shear rate; (**b**) log shear stress vs. log shear rate.

The observed rheological properties of the model facial serums show a non-linear trend between viscosity and shear stress with respect to increasing shear rates. This characteristic behavior is representative of non-Newtonian fluid dynamics, a common feature identified in all tested facial serum formulations.

The addition of grapevine bud extract to the formulation of facial serums, instead of a pure extraction medium, resulted in an increase in apparent viscosity. This suggests that the extract is rich in bioactive compounds that contribute to the overall rheological profile of the formulations under development. The highest apparent viscosity was observed for the facial serum based on grapevine buds' micellar extract, indicating the highest amount of bioactive compounds extracted via micellar extraction from grapevine buds. The high concentration of active ingredients influenced the product viscosity. On the other hand, incorporating a pure solvent or pure micellar solution in the designed formulations during the LCE process had relatively little effect on apparent viscosity, as indicated by marginal significance ($p > 0.05$).

The observed relationship of shear stress increase with increasing shear rate in the model facial serum was fitted to the power-law model (Equation (4)), providing a quantitative representation of the rheological properties of the tested products.

$$H = K\dot{\gamma}^{n-1} \quad (4)$$

where η represents the apparent viscosity (mPa·s), $\dot{\gamma}$ is the shear rate (s^{-1}), n is the flow behavior index (dimensionless), and K is the consistency index ($Pa \cdot s^n$). In the context of pseudoplastic fluids, the flow behavior index (n) is less than 1 [64–66]. Table 6 shows the parameters of the power-law model for the examined model facial serums.

Table 6. Fit parameters to the power-law model of investigated facial serums.

Sample	n	K	R^2
FS_Solv	0.17	7.508	0.9848
FS_SolvE	0.15	8.476	0.9953
FS_Surf	0.15	7.966	0.9895
FS_SurfE	0.13	9.115	0.9952

Comprehensive rheological analysis of the flow characteristics of developed facial serums offers valuable information essential for optimizing formulations and product development in the cosmetic industry. The non-Newtonian properties, shear thinning properties, and the influence of specific ingredients contribute to a deeper understanding of the fluid dynamics governing these formulations, paving the way for the better design and performance of cosmetic products.

3.5.3. Microbiological Stability

Cosmetic products must maintain their safety throughout their designated shelf life, as determined by the manufacturer. The model facial serums were assessed for microbiological stability. The tests yielded no bacterial colonies, fungi, yeasts, or molds. All tested grapevine extracts and facial serums demonstrated the necessary microbiological stability.

3.5.4. Chemical Stability

In order to ensure high quality and consumer safety, the developed facial serums were evaluated for chemical stability using a mechanical loading test. The degradation of the active ingredients in cosmetic preparations can result from environmentally influenced chemical reactions such as oxidation, hydrolysis, isomerization, or decarboxylation. Such changes significantly affect the stability and overall perception of cosmetic products. Organoleptic factors (such as overall appearance, color, and odor) and physicochemical parameters (including pH value, viscosity, weight, and signs of separation) were evaluated in the chemical stability test. No visual changes were observed for all parameters tested; hence, all designed facial serums were assessed as stable.

4. Conclusions

Nowadays, the cosmetics industry is experiencing significant growth, fostering a heightened demand for novel ingredients, particularly those derived from natural sources. The utilization of grapevine buds, cultivated from waste material generated in wine production, emerges as a valuable reservoir of phytochemicals for cosmetics formulations. This not only contributes to the industry's expansion but also aligns with principles of environmental and economic sustainability.

This study provided a comprehensive assessment of the potential use of loan chemical extraction in the cosmetic industry. Micellar and solvent LCE were studied as a tool for the development of natural skin care cosmetics containing substances isolated from grapevine buds.

The results highlight the antioxidant activity of the formulated compositions, emphasizing their ability to protect the skin against adverse environmental influences. The demonstrated biological activity of compounds derived from grapevine buds favorably

positions them as sources of bioactive phytochemicals for cosmetic applications, providing an effective and environmentally friendly alternative to handling resulting residues.

Furthermore, this study culminated in the creation of model facial serums skillfully developed using the loan chemical extraction technique. These model products showcased enhanced benefits for skincare. The work demonstrated that the developed cosmetic preparations, based on the obtained extracts, do not induce cytotoxic effects on keratinocytes in vitro. Furthermore, the addition of extract is capable of mitigating the cytotoxic effects of both the solvent and the surfactant used.

In summary, the adoption of the loan chemical extraction technique in the production of facial serums significantly elevates the safety standards of such formulations, thereby enhancing overall product quality. Moreover, the study sheds light on an intriguing prospect—the utilization of waste generated in wine production for valuable cosmetic purposes.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app14041420/s1, Table S1: The MS/MS transitions and compounds' characteristic parameters for quantified compounds; Figure S1: Extracted ion chromatograms (XIC) obtained for selected compounds in SurfE in negative ionization mode; Figure S2: Extracted ion chromatograms (XIC) obtained for selected compounds in SolvE in negative ionization mode.

Author Contributions: Conceptualization, Z.H.-B. and T.W.; methodology, Z.H.-B., T.W., M.Z., N.S-W., M.T. and M.Z.-D.; validation, Z.H.-B., T.W., M.Z., N.S.-W., E.Z.-T. and M.Z.-D.; formal analysis, Z.H.-B., T.W., M.Z., N.S.-W., E.Z.-T. and M.Z.-D.; investigation, Z.H.-B., T.W., M.Z., N.S.-W. and M.Z.-D.; resources, Z.H.-B., T.W., M.Z., N.S.-W. and M.Z.-D.; data curation, Z.H.-B., T.W., M.Z., N.S.-W. and M.Z.-D.; writing—original draft preparation, Z.H.-B., T.W., M.Z., N.S.-W., E.Z.-T., M.T. and M.Z.-D.; writing—review and editing, Z.H.-B., T.W., M.Z., N.S.-W., E.Z.-T., M.T. and M.Z.-D.; visualization, Z.H.-B., T.W., M.Z., N.S-W. and M.Z.-D.; supervision, Z.H.-B. and T.W.; project administration, Z.H.-B. and T.W.; funding acquisition, Z.H.-B. and T.W. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

The following abbreviations are used in this manuscript:

FS_Solv	Facial Serum without extract (solvent extraction)
FS_SolvE	Facial Serum with extract (solvent extraction)
FS_Surf	Facial Serum without extract (surfactant extraction)
FS_SurfE	Facial Serum with extract (surfactant extraction)

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