Article

Ecodesigned Formulations with Tomato Pomace Extracts

Aya Jamaleddine [1], Martine Urrutigoïty [2], Jalloul Bouajila [3], Othmane Merah [1,4,*], Philippe Evon [1] and Pascale de Caro [1,*]

1 Laboratoire de Chimie Agro-Industrielle (LCA), Université de Toulouse, INRAE, Toulouse INP, 31030 Toulouse, France
2 Laboratoire de Chimie de Coordination (LCC), Université de Toulouse, CNRS, Toulouse INP, 31030 Toulouse, France
3 Laboratoire de Génie Chimique, Université de Toulouse, CNRS, Université Paul Sabatier, 31062 Toulouse, France
4 Département Génie Biologique, Université de Toulouse, Université Paul Sabatier, Institut Universitaire Technologique A, 32000 Auch, France
* Correspondence: othmane.merah@ensiacet.fr (O.M.); pascale.decaro@ensiacet.fr (P.d.C.)

Abstract: Tomato pomace (TP) has previously been identified as a coproduct that is rich in bioactive molecules, with potential beneficial effects for health. For tomato pomace that is composed of the skin, seeds and fibers, the challenge is to recover the molecules of interest trapped in the biopolymers. The use of deep eutectic solvents to extract metabolites from vegetable materials could present some advantages. Four natural deep eutectic solvents (NaDESs) were synthesized and characterized by infrared spectroscopy, thermogravimetry (TG) and differential scanning calorimetry (DSC). The TP was treated by maceration at moderate temperatures with the NaDESs. We identified 39 extracted molecules by HPLC–DAD, which revealed an abundance of hydroxy/methoxy flavones, flavanols, flavonols, phenolic acids, carotenoids and tannins, as well as a certain selectivity in the extracted molecules. Four cosmetic formulations that included the NaDESs were prepared. The NaDESs showed film-forming properties, which were harnessed for the final formulations, thanks to their biocompatibilities. Finally, the coupling of the extraction and formulation is a way to preserve the quality of the extracts and prepare ecodesigned formulations.

Keywords: tomato pomace; ecoextraction; bioactive molecules; formulation; ecodesign

1. Introduction

Currently, there is a strong market trend for products that are formulated with natural and healthier ingredients. This context presents an opportunity to develop innovative products using ecocompatible processes that can preserve the natural molecules. Residual biomass represents a significant source of secondary metabolites, which can be recovered by implementing green processes in accordance with the naturalness of the targeted formulations. Thus, the field of cosmetics is continuously looking for active plant ingredients to respond to the different specifications of skin care products. In this area, the raw materials are carefully selected according to their origins, qualities, properties and costs. A study by Soto et al. [1] showed that the ethanolic extracts of grape pomace, pine (*Pinus pinaster*) wood chips, *Acacia dealbata* flowers and shiitake (*Lentinus edodes*) meet the efficacy expectations when they are formulated for personal skin care products. Indeed, the use of agricultural byproducts represents a source of available metabolites, which avoids the use of dedicated cultures. These new supply chains have reduced ecological footprints and contributed to the better management of biomass waste. Obviously, the microbiological quality of the agricultural coproducts and the presence of pesticide residues must be controlled [2].

To illustrate the role of a coproduct in a formulation, Plainfossé et al. [3] used a hydroalcoholic extract of blackcurrant pomace to develop an antiaging cosmetic base. The work of Carriço et al. [4] has shown that phenolic acids extracted from *Quercus suber* bark,

which is a coproduct of the forestry industry, have interesting potential for preparing creams with antioxidant, antiaging and anti-inflammatory properties. Previous works have also identified tomato pomace as a source of bioactive molecules. For instance, Jamaleddine et al. [5] detected the in vitro bioactivities for fractions isolated by maceration in ethanol or ethyl acetate, and for an extract obtained with SC-CO$_2$. Lycopene extracted from tomato skins and added to an emulsion had a protective effect against photodamage to the skin induced by UVB rays [6]. Nonmarketable tomatoes, powdered after drying, are used in cosmetic formulations as sources of vitamins A, B and C, folic acid, and phytosterols [7].

The usual extraction methods consist of putting the plant material into contact with a solvent (water or organic). This step is followed by the separation of the residual material and the solvent (filtration, centrifugation, etc.), and then the evaporation of the solvent to obtain the extract. The latter, possibly purified, must then be resolubilized to be formulated. To reduce the number of steps and the problems of solubility, and to avoid costly safety requirements, volatile solvents are avoided. Salem et al. [8] obtained fractions rich in polyphenols via the hydroglycerin extraction of grape seeds (i.e., grape pomace) at 40 °C for 2 h. The glycerin medium was used for the formulation of a cream with antioxidant properties.

Among the promising green solvents, deep eutectic solvents (DESs) have some advantages, and some authors have started to test them for extractions of natural molecules [9]. The use of DESs for cosmetic formulations is interesting because of their viscosity and chemical stabilities. Odorless and colorless, they can positively contribute to a formulation's properties. We can cite the work of Huang et al. [10], who extracted rutin-rich fractions from wheat bran using a natural DES (NaDES) from the association between choline chloride and glycerol. Panic et al. [11] isolated anthocyanins from grape pomace using a NaDES composed of choline chloride and citric acid on a half-liter scale, and they succeeded at recycling it. These solvents have undergone significant developments in recent years [12]. Indeed, they have been adapted to cosmetic applications. They are nonvolatile, nontoxic, colorless and recyclable, with high thermal stability [13]. They can be easily prepared by mixing a hydrogen bond donor (HBD) compound and hydrogen bond acceptor (HBA) compound in a certain molar ratio [14]. For eutectic compositions, the mixtures have lower melting points compared with those of the compounds taken separately. Popovic et al. [15] tested a NaDES ("choline chloride: malic acid") combined with microwave activation to extract anthocyanins from cherry pomace. Regarding tomato pomace, we can cite four recent studies. First, Silva et al. [16] and Lazzarini et al. [17] improved the extraction yields of carotenoids using the mixtures "DL-menthol /lactic acid" or "ethyl acetate/ethyl lactate", following the nonthermal air-drying of the tomato pomace. Vorobyova et al. [18] used a choline chloride-based DES to extract phenolic acids from TP (65 °C, 60 min), and they assessed their antioxidant activities. Vasyliev et al. [19] showed that a second DES, which was rich in phenolic acids and flavanols, could be used in a cream formulation with antifungal properties. Chlorogenic acid was detected as the most abundant phenolic acid in the extracts.

The objective of this work was to use tomato pomace as a source of beneficial molecules by trapping them in NaDESs. These extracting matrices could optimize the bioavailability of pomace metabolites. Therefore, the performances of four NaDESs were compared. To avoid the separation of the metabolites from the NaDESs, the feasibility of keeping the NaDES components in the formulations was studied. The extracted metabolites were analyzed by HPLC before their integration into a film-forming formulation.

2. Materials and Methods

2.1. Reagents

The DL-menthol (2-isopropyl-5-methylcyclohexanol (95%)), lactic acid solution (2-hydroxypropionic acid (85–90%)), D-glucose (99%), L-proline (99%) and chitosan were purchased from Sigma Aldrich. The standard compounds used for identification

were purchased from Extrasynthese (Genay, France). Pharmaceutical-grade glycerin (>99%), xanthan gum and Cosgard (a preservative based on benzylic alcohol) were bought from Aroma-Zone.

2.2. Preparation of Tomato Pomace

Fresh tomato pomace was supplied by the "Les Jus du Soleil" cooperative (Marmande, France). The tomato pomace was oven-dried at 50 °C for 8 h to obtain a material with 2%. Before extraction, the TP was ground with an electric grinder to obtain particles with diameters between 1 and 2 mm (measured with optical microscopy (magnification: 10×)).

2.3. Extraction with Glycerol/Glucose Mixture

The DES "glycerol/glucose" preparation was adapted from Wils et al. [20]. Glycerol and glucose were weighed and mixed at the molar ratio (3:1) with 30% water in a 100 mL flask. The mixture was vigorously stirred at 80 °C until the formation of a homogeneous liquid (2 h). Briefly, 2 g of TP was placed in a bottom flask before adding 32 g of DES, and then it was stirred at 600 rpm at 40 °C for two hours. Centrifugation (12,300 rpm, 20 min) led to the separation of the pomace from the NaDES.

2.4. Extraction with DL-Menthol/Lactic Acid Mixture

The preparation of the NaDES "DL-menthol/lactic acid" (Men-Lac) was adapted from Silva et al. [16]. Solid DL-menthol and lactic acid solution was weighed in a glass vial at the molar ratio (8:1). The mixture was heated using a mechanical stirrer at 1200 rpm at 40 °C until the obtainment of a homogeneous medium. Briefly, 3.4 g of TP was added to 20 g of the Men-Lac mixture and mixed at 50 °C for 1.5 h in a water bath. After centrifugation (12,300 rpm, 20 min), the red-colored Men-Lac separated from the pomace particles.

2.5. Extraction with Lactic Acid/Glucose Mixture

The preparation of the "lactic acid/glucose" NaDES was adapted from Fernandez et al. [21]. The lactic acid and glucose, weighed according to the molar ratio (5:1), were mixed under the addition of 15% water and kept at 50 °C for 1 h with magnetic stirring until the formation of a homogeneous and transparent liquid. Briefly, 2 g of TP was suspended in 40 mL of the lactic acid/glucose mixture and homogenized by a vortex for 15 s. The suspension was subjected to ultrasound (power: 200 W; frequency: 20 kHz) at 40 °C for 1 h. Then, the mixture was centrifuged for 30 min to separate the TP particles.

2.6. Extraction with L-Proline/Glycerol Mixture

The NaDES "L-proline/glycerol" preparation was adapted from Wu et al. [22], with some modifications. The two compounds were mixed at the molar ratio (1:2.5) with 30% water and kept under magnetic stirring at 80 °C until the formation of a homogeneous and transparent liquid. Briefly, 2 g of TP was mixed with 20 mL of the prepared DES and kept at 40 °C, with an ultrasonic power of 320 W, for 1 h. The supernatant was obtained by centrifugation at 10,000 rpm for 10 min.

2.7. Thermal Analyses

The TGA/TDA analyses of the NaDESs were carried out with TGA/DSC 3+ equipment (Mettler-Toledo, Viroflay, France). The differential scanning calorimetry (DSC) analyses were performed with DSC Sirius equipment (Netzsch, Selb, Germany). A total of 10.5 mg of the material was placed in an aluminum pod. The nitrogen flow was set at 50 mL/min, with a temperature increase of 10 °C/min between 20 and 600 °C for the thermograms, and between −100 and 20 °C for the calorimetry.

2.8. Fourier-Transform Infrared (FTIR) Analyses

The FTIR spectra of the NaDESs were performed in the range of 600–4000 cm^{-1} with a PerkinElmer Spectrum 100 spectrophotometer using an ATR device. The baseline was corrected, and the absorbance was normalized between 0 and 1.

2.9. High-Performance Liquid Chromatography Analysis (HPLC–DAD)

The HPLC analyses were performed with a Thermo Fisher Scientific Spectra System C18 100 pump equipped with an ACCELA Detector PDA. The separations were achieved on a 150 × 2.1 mm RPC18 reverse phase column (Phenomenex, Le Pecq, France) with a particle size of 3 μm. The elution was performed at a flow rate of 1.2 mL/min, and using a mobile phase that consisted of acidified water at a pH of 2.6 (solvent A) and acidified water:acetonitrile (20:80 *v/v*) (solvent B). The samples were eluted with the following linear gradient: from 12% B to 30% B for 15 min; from 30% B to 50% B for 2 min; from 50% B to 99.9% B for 3 min; from 99.9% B to 12% B for 10 min. The samples were prepared by taking 0.5 g of the NaDES diluted in 1 mL of acetonitrile and filtered with a Millex-HA (0.45 μm pores) syringe filter (Sigma Aldrich, Saint Louis, MI, USA). Three hundred milliliters of each sample were injected, and the detection was registered at 280 nm. The compounds were identified based on their retention times (RTs) and spectral characteristics relative to the standards.

2.10. Determination of Compositions of Extracts

2.10.1. Total Flavonoid Content (TFC)

The flavonoid contents of the extracts in the DESs were determined according to the aluminum chloride method as per Quettier-Deleu et al. [23], with some modifications. Two hundred microliters of the extract in the NaDES and eight hundred microliters of ethanol were put into a flask. One milliliter of a methanolic solution of aluminum chloride (2%) was added and mixed before incubation in the dark for 1 h at room temperature. The absorbance of the samples was measured at 415 nm using a UVD 1800 spectrophotometer (Shimadzu, Kyoto, Japan). A blank was prepared by replacing the extract solution with ethanol, before reading the absorbance. A calibration curve was prepared using rutin as a standard, with concentrations between 0 and 35 μg/mL in ethanol. Two hundred microliters of each DES were added to ensure the same ethanol/DES ratio. The aliquots of the rutin solution were put in contact with the aluminum chloride solution, using the same protocol. The concentrations in the flavonoids were expressed in milligrams of rutin equivalents (REs) per gram of byproducts.

2.10.2. Total Carotenoid Content (TCC)

A UV 1800 spectrophotometer (Shimadzu, Kyoto, Japan) was used to estimate the total carotenoid contents at 446 nm in a quartz cell with a path length of 1 cm. The absorbances at 446 nm of the solutions prepared with concentrations between 1.04 and 26 μg/mL of β-carotene in DES 2 (DL-menthol/lactic acid) were measured. The values obtained were used as a calibration curve. The total carotenoid content was calculated in milligrams of β-carotene equivalents per gram of byproducts.

2.10.3. Total Phenolic Content (TPC)

The total polyphenol contents of the extracts in the DESs were determined using the Folin–Ciocalteu reagent. In a 6 mL tube, 100 μL of 10% (*w/v*) Folin–Ciocalteu reagent was mixed with 1040 μL of DES 3 (lactic acid/glucose) after extraction. After a soft shaking (5 min), 800 μL of a sodium carbonate solution (2%) was added. After manual stirring, the medium was incubated in the dark at room temperature for 30 min. A blank was prepared in a similar manner by replacing the DES with ethanol. The absorbance was measured at 760 nm using a UVD 1800 spectrophotometer (Shimadzu, Kyoto, Japan). Gallic acid was used as a standard for the preparation of a calibration curve, with DES 3 concentrations between 0 and 100 μg/mL. The different solutions of gallic acid were mixed with 100 μL of

Folin–Ciocalteu reagent and incubated in the dark for 30 min. The results are expressed in milligrams of gallic acid equivalents (GAEs) per gram of byproducts.

2.11. Preparation of Cosmetic Emulsions

2.11.1. Formulation of Peel-Off Mask

The "glycerol/glucose" mixture after extraction was used for the formulation of the peel-off mask. The water and polyvinyl alcohol were mixed at 80 °C with constant stirring until the gel formation. The mixture was cooled to 40 °C. Then, the polyethylene glycol 40 (PEG) and the extract in the NaDES were added. Finally, laurate monoglyceride, ethanol and Cosgard were added under vigorous stirring for a few minutes.

2.11.2. Formulation of Lip Balm

The "DL-menthol/lactic acid" mixture, including the extract, was used for the formulation of the lip balm. Candelilla wax, beeswax, NaDES, fractionated coconut oil (caprylis) and castor oil were mixed in a beaker and stirred in a water bath at 40 °C until the formation of a gel.

2.11.3. Formulation of Hydrosoluble Mask

The NaDES lactic acid/glucose, including the extract, was used for the formulation of the gel mask. Xanthan, glycerol, niacinamide and the NaDES were mixed at room temperature before adding the water and Cosgard. The formulation was mechanically stirred for 15 min until the formation of a homogeneous gel. Two drops of lemon essential oil can be added.

2.11.4. Formulation of Moisturizing Cream

The NaDES glycerol/L-proline, including the extract, was used in the formulation of the emulsion. The aqueous and oily phases were prepared separately. Water, the NaDES and xanthan gum were stirred at 80 °C until a homogeneous mixture was obtained. Jojoba oil, glycerin laurate, shea butter and carnauba wax were stirred at 80 °C until homogenization. The oily phase was gradually added to the aqueous phase under stirring at 80 °C for 10 min. After adding starch and ethanol under stirring, the medium thickened, leading to the final emulsion.

3. Results and Discussion

3.1. Synthesis of Deep Eutectic Solvents

We chose to synthesize four deep eutectic solvents to perform the extraction of metabolites from tomato pomace (Table 1). These NaDESs had already been used for the extraction of natural molecules, but two of them have never been applied to tomato pomace. The addition of water in some eutectic solvents helped to adjust the viscosity.

As shown in the table, the glucose/glycerol mixtures were used to extract fatty acids and pigments from spirulina microalgae, and the resulting mixture showed anti-inflammatory activity towards skin keratinocytes [20]. We used the hydrophobic DL-menthol/lactic acid mixture to extract the fractions rich in lycopene from the tomato pomace at 60 °C for 30 min [16]. Fernandez et al. [21] applied the glucose/lactic acid mixture with 15% water under ultrasound (60 min) to several industrial byproducts, including tomato pomace. These conditions represent the optimized solution found by the authors. The mixture allowed for the extraction of both polyphenols and low-polar molecules. We also selected the glycerol/L-proline mixture, which was previously used to extract a combination of phenolic compounds and flavonoids from *Moringa oleifera* L. *leaves* at 40 °C [22]. The same ratios between the hydrogen donor compound and hydrogen acceptor compound were maintained for our experiments.

Table 1. Compositions of selected DESs.

No.	Composition	Molar Ratio	% of Water	Target Molecules/ Plant Matter	Ref.
DES 1	Glycerol + glucose	3:1	30	Fatty acids and pigments/microalga spirulina	[20]
DES 2	DL-menthol + lactic acid	8:1	0	Lycopene/tomato pomace	[16]
DES 3	Glucose + lactic acid	5:1	15	Phenolic compound/tomato pomace, olive cake	[21]
DES 4	Glycerol + L-proline	1:2.5	30	Phenolic compound/moringa leaves	[22]

3.2. Extraction of Tomato Pomace by DESs

The ground tomato pomace was brought into contact with one of the DES under stirring and moderate heat (Figure 1). The solid material was separated by centrifugation before the analyses of the metabolites. The DESs containing the metabolites were then integrated into the formulations.
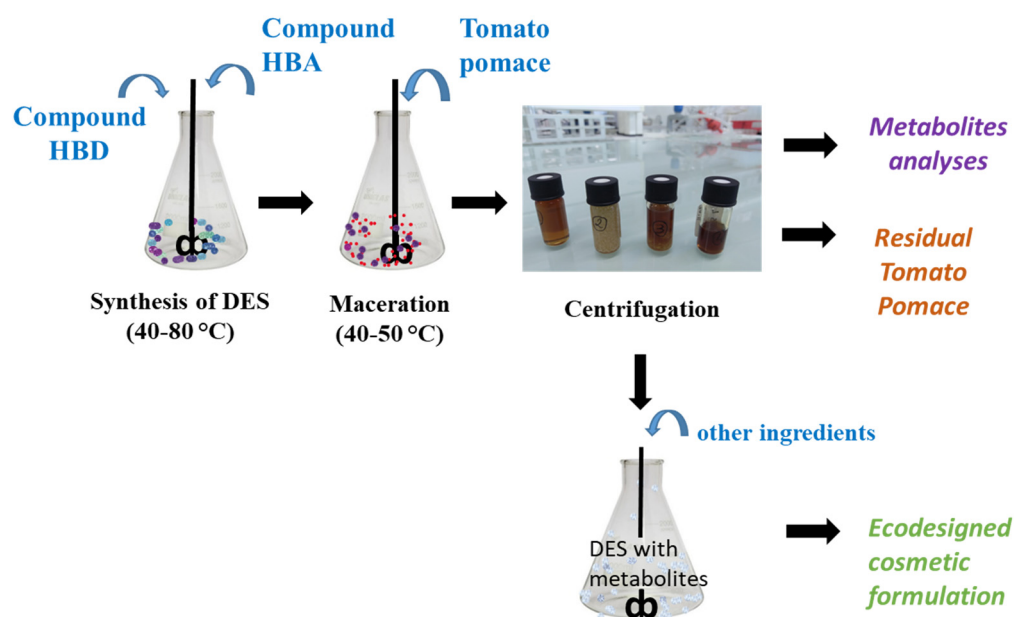
Figure 1. Strategy of extraction/formulation coupling.

The extraction conditions gathered in Table 2 are based on the references in Table 1.

Table 2. Extraction conditions with DESs.

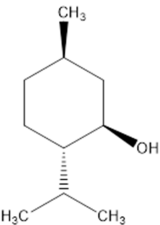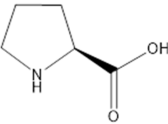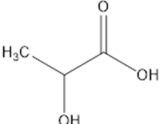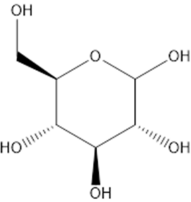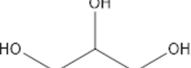| No.	Method of Extraction	Amount of DES	Mass of TP (g)
DES 1	Maceration (2 h, 40 °C)	32 g	2
DES 2	Maceration (30 min, 50 °C)	20 g	3.4
DES 3	Ultrasound (1 h, 40 °C)	40 mL	2
DES 4	Ultrasound (1 h, 40 °C)	20 mL	2

3.3. Characterization of Synthesized NaDESs

3.3.1. Infrared Analyses

The infrared spectra of the NaDESs allowed for the identification of the bands representative of the electronic interactions between the two compounds (Table 3).

Table 3. Formula of molecules used in composition of synthesized NaDESs.

Formula	Molecule
	DL-menthol
	L-proline
	Lactic acid
	D-Glucose
	Glycerol

The formation of the NaDESs was highlighted by the shift in the vibration bands of the bonds that involve heteroatoms. Theses shifts were due to the electronic interactions between the components in the NaDESs. For DES 1 and DES 3, a band due to the angular deformation of the OH group of water molecules appeared at 1645 cm^{-1}. This peak was observed by Santana et al. [24] for several NaDESs containing water. For DES 1, DES 3 and DES 4, the formation of hydrogen bonds involving the OH groups (and NH groups for DES 4) within the NaDESs resulted in shifts in the OH (or NH) extension vibration bands towards lower frequencies. For DES 3 and DES 4, the vibration bands of the C=O bond were widened by the formation of hydrogen bonds with the oxygen atom, which is a phenomenon that was observed by Ali et al. [25] for a DL-menthol/caprylic acid mixture. It was observed for υ(C=O) = 1716 cm^{-1} of lactic acid, and for υ(C=O) = 1609 cm^{-1} (amide II) of L-proline.

The infrared spectra of each NaDES helped to verify that the crystalline structure of the precursors had changed into a glassy nonordered phase.

3.3.2. Thermal Analyses

To synthesize the NaDESs and use them for the extraction, it was necessary to know their stabilities as a function of the temperature. The thermal properties are influenced by the nature of the precursors, the water content and the strength of the interactions

between the molecules. The decomposition temperatures (T_d) determine the temperature range of use. Differential scanning calorimetry indicates the characteristic glass transition temperatures (T_g).

Ribeiro et al. [26] studied the mixture DL-menthol:lactic acid (2:1), for which they measured a decomposition temperature of 229 °C and a glass transition temperature of −61 °C. Craveiro et al. [27] observed a reduction in the glass transition by adding water to a mixture of choline chloride:xylose (2:1) (approximately 4 °C for 5% of added water).

The thermograms of the four NaDESs prepared were carried out between 20 and 600 °C to obtain the mass loss profiles as a function of the temperature. Differential scanning calorimetry covers a temperature range from −100 to 40 °C. The information related to the temperature profiles is presented in Table 4.

Table 4. Results of thermal analyses of NaDESs.

NaDES	Composition	% of Water	T_d (°C)	T_g (°C)	T_c (°C)	T_m (°C)
DES 1	Glycerol/glucose (3:1)	30	180			
DES 2	DL-menthol/lactic acid (8:1)	0	120	−54	−15	≈10
DES 3	Glucose/lactic acid (5:1)	15	130	−75.1		
DES 4	Glycerol/L-proline (1:2.5)	30	180	−66.4		

T_d: decomposition temperature; T_c: crystallization temperature; T_g: glass transition temperature; T_m: melting temperature.

The synthesized NaDESs were stable up to 120, 130 or 180 °C, depending on the constituents. The highest thermal stability was measured for DESs 1 and 4, with T_d = 180 °C. Delgado-Mellado et al. [28] observed that this temperature is generally intermediate between the decomposition temperatures of the pure constituents. As reported by Dai et al. [13], NaDESs that contain sugars, such as DES 1 and DES 3, have decomposition temperatures below 200 °C. DES 2 of the composition 8:1 had a glass transition temperature close to −54 °C, and a subsequent exothermic crystallization peak at −15 °C (−7.8 J/g). We also observed a melting point at 10 °C (7.7 J/g), which is the temperature below the two melting points of the DL-menthol (27 and 34 °C for the polymorphic forms α and β) mentioned by Ribeiro et al. [26].

The glass transition temperatures determined for DES 2, DES 3 and DES 4 were below −50 °C and constituted evidence of synthesized NaDESs. These temperatures attest that NaDESs are supramolecular complexes with stable liquid phases over a fairly wide temperature range [24].

3.4. Analysis of Extracts

The total contents of phenols (TCP) were determined in the DESs after extraction (Table 5). Some components of the DESs reacted with the Folin's reagent (the solution turned blue), which invalidated the measurements for DES 1 (glycerol/glucose), DES 2 (DL-menthol/lactic acid) and DES 4 (glycerol/L-proline). For DES 3, it was observed that the level of polyphenols extracted (1915.5 μg/g of TP) was higher than that measured in an extract made with ethyl acetate (786.7 μg polyphenols/g TP), but it was significantly lower than those obtained with a polar solvent and supercritical CO_2.

Table 5. Comparison of extracted polyphenol rates from tomato pomace.

Solvent of Extraction	Rate of Extracted Polyphenols (μg Gallic Acid Equivalent/g of Dried TP)
DES 3 (lactic acid/glucose)	1915.5 ± 15.1
Ethanol *	3489.5 ± 23.3
Ethanol + water *	3251.8 ± 19.4
Supercritical CO_2 *	3062.9 ± 21.6
Ethyl acetate *	786.7 ± 8.3

* Values obtained from [5].

The total flavonoid contents (TFCs) presented in Table 6 show that DES 3 (lactic acid/glucose) had the highest level of extracted flavonoids (1410.9 µg/g TP) compared with the other DESs. DES 2 is better suited to the extraction of apolar molecules. According to the results obtained, ethanol remained the most appropriate solvent for extracting this category of compounds (3479 µg of flavonoids/g of TP).

Table 6. Comparison of extracted flavonoid rates from tomato pomace.

Extraction Solvent	Rate of Extracted Flavonoids (µg Rutin Equivalent/g of TP)
DES 1	439.5 ± 8.3
DES 2	50.5 ± 5.3
DES 3	1410.9 ± 15.3
DES 4	893.5 ± 10.8
Ethanol	3479 ± 25.5
Ethanol + ethyl acetate	1853.2 ± 13.4
Supercritical CO_2	1174.8 ± 12.3

Fernandez et al. [21] found DES 3 interesting for phenolic acid extraction. Indeed, the HPLC analyses confirmed that DES 3 is particularly rich in gallic acid and chlorogenic acid. The DES "choline chloride: lactic acid" was also reported to be efficient with 51.7 mg GAE/g extract from tomato pomace [18]. Nevertheless, the NaDES did not improve the rate of extraction obtained with ethanol (Table 6).

The levels of carotenoids extracted were determined using spectrophotometry (Table 7). DES 2 (DL-menthol/lactic acid) is suitable for the extraction of carotenoids, as confirmed by the COSMO-RS predictions of Vasiliev et al. [19]. We found a rate of 96.4 µg carotene/g TP with this DES, which is lower than the 1446.6 µg lycopene/g MS obtained by Silva et al. [16] under similar conditions. Lazzarini et al. [17] showed the influence of the drying process of tomato pomaces on the extraction rates of carotenoids, which could explain this difference. The extraction made using SC-CO_2 had the highest rate of carotenoid extraction.

Table 7. Comparison of extracted carotenoid rates from tomato pomace.

Extraction Solvent	Rate of Extracted Carotenoids (µg β-Carotene Equivalent/g of TP)
DES 2	96.4 ± 4.1
Supercritical CO_2	2895.1 ± 26.2
Ethanol + ethyl acetate	1521.0 ± 17.4
Ethyl acetate	1293.7 ± 15.5
Ethanol	849.6 ± 12.3

The metabolites extracted by the DESs were also analyzed via HPLC–DAD at 280 nm (Figure 2). The 39 molecules identified are listed in Table 8. The comparison of the area unit of the peaks for the same molecule indicated that **DES 4** was dominated by flavanols/flavonols (molecules **2, 8, 11** and **17**), flavones (molecules **20, 24, 28, 31, 34** and **37**) and naringenin (flavanone). In the same way, the total phenolic content (TPC) of **DES 3** can be attributed to its high contents of chlorogenic acid (molecule **6**) and gallic acid (molecule **1**). Compared with the other DESs, **DES 1** is characterized by high contents of ferulic acid, p-coumaric acid, tannins (molecules **9, 10, 15** and **39**), flavones (molecules **14** and **30**) and flavonols (myricetin and quercetin). As expected, the content of carotenoids was higher in **DES 2**, which also contained some flavones (for instance, molecule **38**).
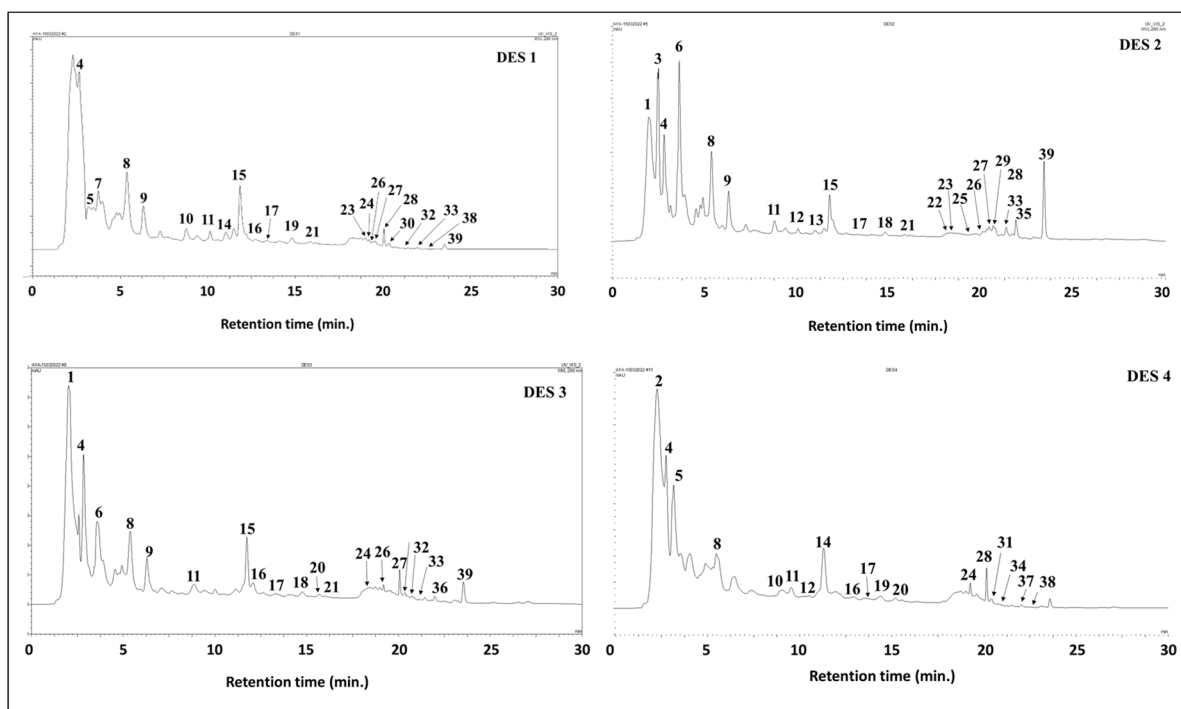
Figure 2. HPLC-DAD chromatograms at 280 nm of media after extraction (extracts in NaDESs).

Many of these molecules confer antioxidant or anti-inflammatory properties (kaempferol, cinnamic acid derivatives, some phenolic acids), which are beneficial for the skin. For example, ferulic acid is not only a free radical scavenger, but it is also an inhibitor of the enzymes that catalyze the generation of free radicals. It has a protective role for the main structures of the skin, and it is interesting for its anti-inflammatory, antioxidant and antimicrobial properties, even if it tends to oxidize quickly [29]. Lycopene is the most abundant carotenoid in tomato pomace, and it has antioxidant properties that act to inhibit UV effects. Moreover, the phytosterols contained in tomato seed oil have restorative and healing properties that are interesting for lip balm [30].

3.5. Methodology of Formulations

For the present work, we chose to keep the whole extracting medium for the formulations to avoid the separation of the molecules from the DESs. This strategy avoided the usual difficulties of resolubilizing an extract into a formulation. The compositions of the selected NaDESs (Table 3) are compatible with cosmetic formulations, as the compounds are listed in the INCI Beauty database. Moreover, they are authorized as organic ingredients by the international COSMOS standard. The role of each compound is specified in Tables 8–10. In a formulation, antioxidant molecules help to delay the oxidation of other molecules by inhibiting chain reactions. They can be endogenous or exogenous molecules. Antioxidants also fight against the formation of reactive oxygen species (ROS) that are produced by metabolism and involved in the skin aging mechanism. In galenic formulations, the use of lycopene, which is a powerful antioxidant, is a very recent approach. Indeed, the changes in the colors and fragrances of the formulations that contain lycopene are no longer perceived as disadvantages, according to a sensory analysis conducted by Costa et al. [31]. As for phenolic acids, they can inhibit the activities of collagenase and elastase, which are enzymes that are involved in the degradation of collagen and elastin, respectively [4]. The same author showed that cork extracts rich in phenolic acids and tannins help to regulate sebum production. Among these compounds (i.e., phenolic acids and tannins), some have shown antimicrobial properties, such as the gallic acid present in NaDESs 2 and 3, which is interesting for the preservation of emulsions.

Table 8. Identification of molecules in tomato pomace extracts by HPLC–DAD (a.u.: area unit).

No.	RT (min)	Compound	DES 1 (a.u.)	DES 2 (a.u.)	DES 3 (a.u.)	DES 4 (a.u.)
1	**2.04**	Gallic acid	-	30.4	**193.3**	-
2	**2.21**	(−)-Epicatechin *(flavanol)*	-	-	-	**456.0**
3	**2.51**	Methyl 3,5-dihydroxybenzoate	-	**17.9**	-	-
4	**2.70**	Ferulic acid	**465.7**	16.9	66.4	124.8
5	**3.15**	Caffeic acid	158.7	-	-	**285.8**
6	**3.65**	*Trans*-3-hydroxycinnamic acid *(chlorogenic acid)*	-	27.5	**72.0**	-
7	**3.85**	p-Coumaric acid	**212.8**	-	-	-
8	**5.43**	Myricetin *(flavonol)*	**237.0**	13.0	44.6	199.7
9	**6.21**	6-Hydroxycoumarin *(tannin)*	**105.8**	6.1	45.1	-
10	**9.18**	2-Hydroxycinnamic acid *(tannin)*	28.8	-	-	**32.7**
11	**9.63**	Quercetin *(flavonol)*	**40.0**	0.9	9.3	21.3
12	**10.61**	3,4-Dihydroxycinnamate	-	0.1	-	**14.6**
13	**10.94**	trans-Cinnamic acid	-	0.4	-	-
14	**11.17**	Naringenin *(flavanone)*	-	-	-	**81.6**
15	**11.77**	α-Cyano-4-hydroxycinnamic acid	**144.2**	4.7	37.0	-
16	**12.66**	Vitamin E *(tocopherol)*	**9.7**	0.1	4.1	5.4
17	**13.8**	Kaempferol *(flavonol)*	0.4	0.1	3.3	3.3
18	**14.68**	3-Cyano-7-hydroxy-4-methyl coumarin	-	0.3	3.8	-
19	**14.99**	2,4-Dihydroxy-3,6-dimethyl benzoic acid	**10.1**	-	-	2.8
20	**15.58**	6-Hydroxy flavone	-	-	1.4	1.2
21	**16.22**	5,6,7-Hydroxy flavone *(baicalein)*	0.9	0.1	0.1	-
22	**18.1**	7-Hydroxy-4-phenylcoumarin	-	0.3	-	-
23	**18.53**	Ethyl *trans*-2-hydroxy cinnamate	**31.7**	1.3	-	-
24	**18.70**	5-Hydroxy-4′-methoxy flavone	14.9	-	15.7	**42.8**
25	**19.61**	7-Hydroxy flavone	-	0.2	-	-
26	**19.79**	β-Carotene	9.2	**24.5**	7.3	-
27	**19.81**	Lutein	0.1	**11.1**	7.3	-
28	**20.28**	5,7-Dihydroxy-3′,4′,5′-trimethoxy flavone	2.9	0.2	-	**15.0**
29	**20.62**	5,7-Dihydroxy-4-propyl coumarin	-	0.3	**0.8**	-
30	**20.75**	3′-Hydroxy-6-methyl flavone	**3.2**	-	-	-
31	**20.99**	5-Hydroxy flavone	-	-	-	0.1
32	**21.12**	3,3′-Dimethoxy flavone	0.2	-	0.2	-
33	**21.49**	3,6,3′-Trimethoxy flavone	0.6	-	0.6	-
34	**21.50**	7-Hydroxy-3′,4′,5′-trimethoxy-α-naphthoflavone	-	-	-	**0.6**
35	**21.83**	3,7-Dimethoxyflavone	1.0	**1.4**	-	-
36	**22**	5-Hydroxy-3′-methoxy flavone	-	-	**1.2**	-
37	**22.03**	5-Hydroxy-4′-methoxy flavone	-	-	-	**0.9**
38	**22.54**	4′,5′-Dimethoxy-2′-hydroxy-4-methyl chalcone	-	-	-	**0.2**
39	**23.39**	Hamamelitannin	**10.2**	5.1	5.02	-

Table 9. Composition of peel-off mask.

Ingredient	Composition (% w)	Function
Polyvinyl alcohol	15.0	Film-forming agent (viscosity control)
Water	69.1	Solvent
DES 1 with extract	11.4	Antioxidant and purifying agent
Polyethylene glycol 40	2.1	Film-forming and thickening agent
Glycerol monolaurate	1.0	Emollient and emulsifier agent
Ethanol	1	Solubilizer and inhibitor of microbial activity
Cosgard	0.4	Preservative

Table 10. Composition of lip balm.

Ingredient	Composition (% w)	Function
Candelilla wax	10.4	Film-forming agent
Beeswax	10.0	Emulsifying, film-forming and perfuming agent
Fractionated coconut oil (caprylis)	46.3	Softener
DES 2 with extract	2.3	Coloring (lycopene) and regenerating agent
Castor oil	30.2	Nourishing and repairing agent
Raspberry extract	7 drops	Natural origin, accepted by ECOCERT

In cosmetics, there are several ways to protect and beautify the skin. The formulations depend on the part of the face concerned (i.e., skin, lips or eyes).

A **mask** offers an effective way to provide the skin with nutrients and ensure the hyperhydration state of the epidermis for an improvement in the skin texture [32]. It can be a water-washable mask or the "peel-off" type, the adhesion of which removes impurities from the skin.

A **lip balm** should moisturize, repair and protect against the cold. Its texture should be pleasant and not sticky. Balms have lipid bases, such as coconut oil. Azmin et al. [33] used this oil to extract lycopene by macerating powdered dried tomatoes.

A **moisturizing cream** has the properties of protecting the skin from external aggressions, such as cold, pollution and UV rays.

The analyses carried out showed that the NaDESs were appropriate for the concentration of some of the bioactive molecules that were present in the tomato pomace. The NaDESs with extracted metabolites were incorporated into two different mask formulations: a cream and a balm (Figure 3).

Figure 3. Cosmetic formulations from left to right: peel-off mask (DES 1); lip balm (DES 2); water-soluble mask (DES 3); cream (DES 4).

Glycerol is a moisturizing agent and glucose is a humectant agent, which means that DES 1 (glycerol/glucose) was compatible with the preparation of a mask (Table 9). The antioxidant and anti-inflammatory activities of the bioactive molecules from the tomato pomace provided the mask with some of the properties that are sought after to cleanse and regenerate the skin. The formulation of the peel-off mask also included a synthetic polymer that is soluble in water so that the mask can form a homogeneous film that adheres to the skin and can be easily removed after the application time.

DES 2 (DL-menthol/lactic acid) was chosen to prepare a lip balm (Table 10) because menthol can be introduced in low doses into lip balm formulations, which provides a refreshing effect. The lactic acid produced by a fermentation process using *Lactobacillus* helped to regulate the pH and bacterial colonization of the preparation. DES 2 is rich in carotenoids and hydroxy flavones, the antioxidant properties of which protect and repair the lips. The texture was solid, and the melting was sufficient to mold it into a stick. It can be easily spread, and it forms a smooth film.

DES 3 (lactic acid/glucose) is suitable for formulating a water-soluble mask (Table 11). The lactic acid helps to adjust the pH for gentle exfoliation. The glucose present in the DES acts as a humectant. The formulation spreads on the skin and forms a film with moderate adhesion [33]. DES 3 is rich in gallic acid and chlorogenic acid, the antioxidant properties of which keep the skin in good condition.

Table 11. Composition of hydrosoluble mask.

Ingredient	Composition (% w)	Function
Xanthan gum	7.5	Gelling agent and emulsifier
DES 3 with extract	5.3	Film-forming agent and antioxidant
Glycerol	20.5	Moisturizing agent
Water	55.7	Solvent
Niacinamide	10	Vitamin B3 and smoothing agent
Cosgard	1.0	Preservative

In DES 4 (glycerol/L-proline), glycerol is a moisturizing agent, and L-proline is one of the 20 amino acids that make up our body's proteins. This amino acid is involved in collagen metabolism and is used as a skin care agent. According to the composition of the cream (Table 12), DES 4 contains powerful antioxidants (such as epicatechin and myricetin, caffeic acid, naringenin), which confer antiaging properties to the cream.

Table 12. Composition of moisturizing cream.

Ingredient	Composition (% by Mass)	Function
Water	40.7	Solvent
DES 4 with extract	18.5	Antioxidant, regenerating properties
Xanthan gum	0.3	Gelling agent, emulsifier
Jojoba oil	11.1	Emollient, skin protection
Carnauba wax	0.9	Emollient
Glycerin laurate	4.1	Softener and emulsifier
Shea butter	3.4	Texturizing agent, skin care
Starch	3.6	Viscosity control
Ethanol	17.2	Solvent

3.6. Application of Formulations

Formulation pH values between 5 and 7 respect the pH of the skin [3]. The drying times were measured on films spread on contrast cards from a deposit of a known mass. They were evaluated for between 5 and 10 min. A spreading test was carried out by depositing 0.07 g of the formulation between two glass slides (Figure 4).

Figure 4. Tests of formulation spreading (0.07 g). From left to right: peel-off mask; water-soluble mask; cream; lip balm.

The spreading diameters of each formulation are shown in Table 13. Logically, the cream, being more fluid, had the highest spreading diameter. The masks had thicker textures, but they formed homogeneous and translucent films. The texture of the balm was more consistent (a solid wax-like formulation), but it melted sufficiently to hug the surface. A drop of the NaDES was also brushed onto a contrast card (2 cm^2), which showed the initial film-forming properties of the NaDES, which probably contributed to the final texture of the formulation (Table 12). The characteristics of the four NaDESs seem favorable for the elaboration of film-forming formulations that include active molecules. The polar molecule solubilization abilities were better for NaDESs 3 and 4. It should also be noted that the costs of NaDESs 1 and 3 (based on the glucose, glycerol and lactic acid) were rather moderate. It is necessary to assess whether the added value of L-proline (for the cream) and DL-menthol (for the balm) can compensate for the respective costs of NaDESs 2 and 4.

Table 13. Film-forming properties of NaDESs and their resulting formulations.

Property	Peel-Off Mask	Water-Soluble Mask	Hydrating Cream	Lip Balm
Aspects of dry film of NaDESs on contrast cards	Glossy film	Soft film	Mat film	Mat and smooth film
Spread diameters of formulations (cm) *	1.5	2	3	1.2

* According to Figure 4.

4. Conclusions

In this article, four eutectic solvents with different polarities and compositions were synthesized. The syntheses were carried out at moderate temperatures (50–80 °C). The NaDES were characterized by infrared spectroscopy and thermal analyses, which highlighted the interactions between the molecules and the formation of a stable liquid phase up to a decomposition temperature > 120 °C. These NaDESs have already been used for the extraction of natural molecules, but two of them have never been applied to tomato pomace.

The results showed that the selected NaDES were suitable for the extraction of the metab-olites present in the tomato pomace. From HPLC data, the extraction ability of NaDES were compared and defined their selectivity towards each molecule. Thus, the DL-menthol/lactic acid mixture (DES 2) preferentially trapped low-polar compounds (carotenoids, lipids, to-copherol), while the glucose/ glycerol mixture (DES 1) showed affinity with some phenolic acids, flavones, flavonols and tannins. The glucose/lactic acid

mixture (DES 3) was particu-larly selective towards some phenolic compounds, while the glycerol/ L-proline (DES 4) was efficient for the extraction of some flavones, flavonols and flavanones. The possibility of com-bining the extraction and formulation steps was achieved, while maintaining the quality of the ingredients. The biocompatibility of these NaDES made it possible to incorporate them into the cosmetic formulations, which represents a new strategy for the ecoconception of formulations. Moreover, the bioactive molecules extracted by the NaDES can really generate beneficial effects for the facial skin and lips, based on the synergetic effects of the metabolites. Further tests should be considered to check the skin tolerance and to assess the antiaging properties of formulations by measuring the inhibition of elastase, collagenase and hyaluron-idase.

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References

1. Soto, M.L.; Parada, M.; Flaqué, E.; Dominguez, H. Personal-Care Products Formulated with Natural Antioxidant Extracts. *Cosmetics* **2018**, *5*, 13. [CrossRef]
2. Barbulova, A.; Colucci, G.; Apone, F. New trends in cosmetics: By-products of plant origin and their potential use as cosmetic active ingredients. *Cosmetics* **2015**, *2*, 82–92. [CrossRef]
3. Plainfossé, H.; Trinel, M.; Verger-Dubois, G.; Azoulay, S.; Burger, P.; Fernandez, X. Valorisation of *Ribes nigrum* L. pomace, an agri-food by-product to design a new cosmetic active. *Cosmetics* **2020**, *7*, 56. [CrossRef]
4. Carriço, C.; Ribeiro, H.M.; Marto, J. Converting cork by-products to ecofriendly cork bioactive ingredients: Novel pharmaceutical and cosmetics applications. *Ind. Crops Prod.* **2018**, *125*, 72–84. [CrossRef]
5. Jamaleddine, A.; Caro, D.P.; Bouajila, J.; Evon, P.; Haddad, J.G.; El-Kalamouni, C.; Hijazi, A.; Merah, O. In Vitro bioactivities of extracts from tomato pomace. *Front. Biosci. (Landmark Ed.)* **2022**, *27*, 259. [CrossRef] [PubMed]
6. Sopyan, I.; Gozali, D.; Tiassetiana, S. Formulation of tomato extracts (*Solanum lycopersicum* L.) as a sunscreen lotion. *Natl. J. Physiol. Pharm. Pharmacol.* **2017**, *8*, 453–458. [CrossRef]
7. Ijaz, N.; Durrani, A.I.; Rubab, S.; Bahadur, S. Formulation and characterization of Aloe vera gel and tomato powder containing cream. *Acta Ecol. Sin.* **2022**, *42*, 34–42. [CrossRef]
8. Salem, Y.; Rajha, H.N.; Franjieh, D.; Hoss, I.; Manca, M.L.; Manconi, M.; Castangia, I.; Perra, M.; Maroun, R.G.; Louka, N. Stability and antioxidant activity of hydro-glyceric extracts obtained from different grape seed varieties incorporated in cosmetic creams. *Antioxidants* **2022**, *11*, 1348. [CrossRef]
9. Ling, J.; Hadinoto, K. Deep eutectic solvent as green solvent in extraction of biological macromolecules: A review. *Int. J. Mol. Sci.* **2022**, *23*, 3381. [CrossRef]
10. Huang, Y.; Feng, F.; Jiang, J.; Qiao, Y.; Wu, T.; Voglmeir, J.; Chen, Z.-G. Green and efficient extraction of rutin from tartary buckwheat hull by using natural deep eutectic solvents. *Food Chem.* **2017**, *221*, 1400–1405. [CrossRef]
11. Panic, M.; Gunjevic, V.; Cravotto, G.; Redovnikovic, I.R. Enabling technologies for the extraction of grape-pomace anthocyanins using natural deep eutectic solvents in up-to-half-litre batches extraction of grape-pomace anthocyanins using NADES. *Food Chem.* **2019**, *300*, 125185. [CrossRef]
12. Li, X.; Row, K.H. Development of deep eutectic solvents applied in extraction and separation. *J. Sep. Sci.* **2016**, *39*, 3505–3520. [CrossRef] [PubMed]
13. Dai, Y.; Spronsen, J.V.; Witkamp, G.J.; Verpoorte, R.; Choi, Y.H. Natural deep eutectic solvents as new potential media for green technology. *Anal. Chim. Acta* **2013**, *766*, 61–68. [CrossRef] [PubMed]

14. Khandelwal, S.; Tailor, Y.K.; Kumar, M. Deep eutectic solvents (DESs) as eco-friendly and sustainable solvent/catalyst systems in organic transformations. *J. Mol. Liq.* **2016**, *215*, 345–386. [CrossRef]
15. Popovic, B.M.; Micic, N.; Potkonjak, A.; Blagojevic, B.; Pavlovic, K.; Milanov, D.; Juric, T. Novel extraction of polyphenols from sour cherry pomace using natural deep eutectic solvents—Ultrafast microwave-assisted NADES preparation and extraction. *Food Chem.* **2022**, *366*, 130562. [CrossRef] [PubMed]
16. Silva, Y.; Ferreira, T.; Jiao, G.; Brooks, M.S. Sustainable approach for lycopene extraction from tomato processing by-product using hydrophobic eutectic solvents. *J. Food Sci. Technol. (India)* **2019**, *56*, 1649–1654. [CrossRef]
17. Lazzarini, C.; Casadei, E.; Valli, E.; Tura, M.; Ragni, L.; Bendini, A.; Toschi, T.G. Sustainable drying and green deep eutectic extraction of carotenoids from tomato pomace. *Foods* **2022**, *11*, 405. [CrossRef]
18. Vorobyova, V.; Skiba, M.; Vasyliev, G. Extraction of phenolic compounds from tomato pomace using choline chloride-based deep eutectic solvents. *J. Food Meas. Charact.* **2022**, *16*, 1087–1104. [CrossRef]
19. Vasyliev, G.; Lyudmyla, K.; Hladun, K.; Skiba, M.; Vorobyova, V. Valorization of tomato pomace: Extraction of value-added components by deep eutectic solvents and their application in the formulation of cosmetic emulsions. *Biomass Convers. Biorefinery* **2022**, *12*, 95–111. [CrossRef]
20. Wils, L.; Leman-Loubière, C.; Bellin, N.; Clément-Larosière, B.; Pinault, M.; Chevalier, S.; Enguehard-Gueiffier, C.; Bodet, C.; Boudesocque-Delaye, L. Natural deep eutectic solvent formulations for spirulina: Preparation, intensification, and skin impact. *Algal Res.* **2021**, *26*, 102317. [CrossRef]
21. Fernandez, M.; Espino, M.; Gomez, F.J.V.; Silva, M.F. Novel approaches mediated by tailor-made green solvents for the extraction of phenolic compounds from agro-food industrial by-products. *Food Chem.* **2018**, *239*, 671–678. [CrossRef] [PubMed]
22. Wu, L.; Li, L.; Chen, S.; Wang, L.; Lin, X. Deep eutectic solvent-based ultrasonic-assisted extraction of phenolic compounds from *Moringa oleifera* L. leaves: Optimization, comparison and antioxidant activity. *Sep. Purif. Technol.* **2020**, *247*, 117014. [CrossRef]
23. Quettier-Deleu, C.; Gressier, B.; Vasseur, J.; Dine, T.; Brunet, C.; Luyckx, M.; Cazin, M.; Cazin, J.C.; Bailleul, F.; Trotin, F. Phenolic compounds and antioxidant activities of buckwheat (Fagopyrum esculentum Moench) hulls and flour. *J. Ethnopharmacol.* **2000**, *72*, 35–42. [CrossRef] [PubMed]
24. Santana, A.P.R.; Mora-Vargas, J.A.; Guimarães, T.G.S.; Amaral, C.D.B.; Oliveira, A.; Gonzalez, M.H. Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods. *J. Mol. Liq.* **2019**, *293*, 111452. [CrossRef]
25. Ali, H.M.; Ghareeb, M.M.; Al-Remawi, M.; Al-Akayleh, F. New insight into single phase formation of capric acid/menthol eutectic mixtures by Fourier-transform infrared spectroscopy and differential scanning calorimetry. *Trop. J. Pharm. Res.* **2020**, *19*, 361–369. [CrossRef]
26. Ribeiro, B.D.; Florindo, C.; Iff, L.C.; Coelho, M.; Marrucho Ferreira, I.M. Menthol-based eutectic mixtures: Hydrophobic low viscosity solvents. *ACS Sustain. Chem.* **2015**, *3*, 2469–2477. [CrossRef]
27. Craveiro, R.; Aroso, I.; Flammia, V.; Carvalho, T.; Viciosa, M.T.; Dionísi, M.; Barreiros, S.; Reis, R.L.; Duarte, A.R.C.; Paiva, A. Properties and thermal behavior of natural deep eutectic solvents. *J. Mol. Liq.* **2016**, *215*, 534–540. [CrossRef]
28. Delgado-Mellado, N.; Larriba, M.; Navarro, P.; Rigual, V.; Ayuso, M.; García, J.; Rodríguez, F. Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR-ATR analysis. *J. Mol. Liq.* **2018**, *260*, 37–43. [CrossRef]
29. Zduńska, K.; Agnieszka, D.; Kolodziejczak, A.; Rotsztejn, H. Antioxidant properties of ferulic acid and its possible application. *Ski. Pharmacol. Physiol.* **2018**, *31*, 332–336. [CrossRef]
30. Lu, Z.; Wang, J.; Gao, R.; Ye, F.; Zhao, G. Sustainable valorisation of tomato pomace: A comprehensive review. *Trends Food Sci. Technol.* **2019**, *86*, 172–187. [CrossRef]
31. Costa, A.M.; Marques, M.; Congiu, F.; Paiva, A.; Simões, P.; Ferreira, A.; Bronze, M.R.; Marto, J.; Ribeiro, H.M.; Simões, S. Evaluating the presence of lycopene-enriched extracts from tomato on topical emulsions: Physico-chemical characterization and sensory analysis. *Appl. Sci.* **2021**, *11*, 5120. [CrossRef]
32. Gupta, S.K.; Scottsdale, A.Z. Skin Firming Anti-Aging Cosmetic Mask Compositions. U.S. Patent US2004/0161435, 19 August 2004.
33. Azmin, S.; Abidin, Z.; Sulaiman, N.S.; Nor, M.; Abdullah, P. Evaluation of moisturizing lip balm comprise of natural pigment from tomato. *AIP Conf. Proc.* **2022**, *2454*, 020028.