Resinoid from cape gooseberry fruit (*Physalis peruviana* L.) – volatile composition and application as an active ingredient in a cosmetic formulation

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Abstract. Cape gooseberry (*Physalis peruviana* L.), an exotic fruit gaining popularity in Bulgaria, has been recognized as a highly functional food, but has also the potential to be a resource for the fragrance and cosmetic industries. The main objective of this study was to assess the potential of the resinoid (a type of traditional aromatic products) obtained from locally-produced fruit (variety "Plovdiv") for use in cosmetics, by revealing its volatile composition and characterizing the properties of an author-developed resinoid- enriched cosmetic cream. The resinoid (yield 58.78% DW) was a dark-orange viscous mass, with fruity, caramel notes and smoke accords odor. The GC-MS analysis identified 44 volatiles (98.69%), representing carbohydrates, alcohols, acids, along with minor miscellaneous compounds. A cosmetic cream (O/W emulsion) was developed, incorporating fruit resinoid (1.00%) as an active ingredient, compared to a control sample. Resinoid inclusion affected positively the sensory and physico-chemical properties of the cosmetic cream (color, odor, pH, stability). The studied emulsions had the rheological behavior of pseudoplastic non-Newtonian fluids, and resinoid presence reduced cream viscosity. It could be concluded that Cape gooseberry fruit resinoid had the potential to be a reasonable ingredient in cosmetic preparations; of course, further research is needed to assess its complex effects.

1 Introduction

The current taxonomy of family Solanaceae (order: *Solanales*), as evidenced by the most recent molecular phylogenetic studies, includes approximately 100 genera and over 2500 species [1]. The Solanaceae species represent many of the most important agricultural crops worldwide, as well as a variety of medicinal plants, ornamentals, herbs, and other species used by men since ancient times, such as potatoes, tomatoes, eggplants, ball and chili peppers, tobacco, tomatillos, petunia, and many others. The genus *Physalis* (subfamily: *Solanoidae*) is one of the six largest genera in the Solanaceae family, with over 85 species originating mainly from the tropical regions of Central and South America. A recent study reported the discovery of 52-milion-year-old fruit fossils from Argentina, ascribed to the genus Physalis, which demonstrated the early Eocene diversification of the family and the ancient origin of the lantern fruit lineage [2]. The genus, distinguished by the accrescent calyces covering the fruit at maturity, includes several species, which produce edible berries, but only a few select species are extensively cultivated worldwide.

The main *Physalis* species of commercial importance include *P. peruviana* L. (Cape gooseberry, Inca berries, pohaberries), *P. philadelphica* Lam. (synonym: *P. ixocarpa* Brot.; tomatillo, Mexican husk tomato) and *P. alkekengi* L. (Chinese lantern, bladder cherry).

P. peruviana, finding its origin in the Peruvian and Ecuadorian Andes, is probably the most widely introduced *Physalis* species worldwide, nowadays cultivated in Central and South Europe, South America, North America, Asia, the Pacific region, *etc.* [3]. Colombia has turned into the centre of Cape gooseberry production, with an annual harvest of over 11.5 million kg fresh fruit [3 - 6].

·*P. peruviana* is gradually gaining popularity in Bulgaria, but it still remains a relatively unfamiliar and exotic fruit in the country. Data suggest rather sporadic Cape gooseberry cultivation and fruit production in Bulgaria, although the awareness of species potential, both as an economic crop and as a functional food, has resulted in the development of an original local variety more than 20 years ago. The first and so far, the only Bulgarian variety of Cape gooseberry, named "Plovdiv", has been created through recurrent selection in a plant population at the Department of Horticulture at the Agricultural University in Plovdiv, in the period between 1996 and 2001, and has been officially recognized in 2006 [7]. The fruit of the Bulgarian variety are characterized with the typical strawberry flavor, combined with slight to medium vanilla hues and a pleasant, mild sweet-to-sour taste [7]. The fruit of the local variety have been

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recognized as fully competitive to the imported Colombian ones in terms of yield, quality and nutrition indices [7, 8]. Fresh fruit have been identified as a low-caloric (with an energy value of 58.25 kcal/100 g) source of functional nutrients – lipids, 1.01%; protein, 2.06%; carbohydrates, 10.23 g/100 g, of which 2.90% reducing sugars, 1.16% pectin, and 4.29% fiber; natural pigments – 3.62 µg/g chlorophylls and 22.36 µg/g carotenoids; macro and microminerals – K, 4876 mg/kg; Mg, 91.42 mg/kg; Fe, 18.51 mg/kg; Zn, 11,78 mg/kg, *etc.* [8]. The locally produced Cape gooseberry fruit are also rich in extractible phenolics, with 5.61 - 14.53 mg GAE/100 g total phenolic content and 0.8 - 9.48 mg QE/100 g total flavonoid content found in different extracts derived from whole fresh fruit [9]. According to the same study, the radical scavenging and metal chelating properties of Cape gooseberry fruit from Bulgaria did not yield to the antioxidant activity of the traded varieties worldwide – DPPH, 106.11 mM TE/100 g; ABTS, 145.2 mM TE/100 g; FRAP, 170.94 mM TE/100 g; and CUPRAC, 342.76 mM TE/100 g [9].

Apart from its significance as a dietetic food, *P. peruviana* fruit, as well as the calyces and the other aerial parts of the plants, have centuries-long history of ethnomedical use in many cultures – for the empirical treatment of diseases like cancer, hepatitis, malaria, asthma, rheumatism; for the reduction of blood glucose and albumin [3, 10]; for the treatment of cough, sore throat, fever, abscesses [11]; as an antipyretic, diuretic, immunomodulator, *etc.* [3]. Contemporary knowledge has supported many of those empirical effects and has validated the traditional use of the species, having revealed different assets of its pharmacological activity and the diversity of its metabolic profile. A number of pure substances or complex pharmacological extracts have been obtained from the fruit and other aerial organs of Cape gooseberry plants, such as concentrated ethanolic fruit extracts rich in carotenoids, phenolic acids, flavonoids, tannins, alkaloids, vitamins (C, B_3, B_6), with antioxidant, antibacterial and anti-tumor effects [12, 13].

In contrast to the achievements in the investigation of the nutritional and pharmacological benefits of Cape gooseberry use, a relatively limited number of studies has been devoted to the identification of individual volatile substances and aroma precursors in *P. peruviana* fruit, although such information is highly important for the food industry and the development of new products from fruits. Solvent extraction, dynamic headspace analysis and headspace solid phase microextraction have been pointed out as the most frequently applied analytical techniques that allow an adequate representation of natural Gape gooseberry fruit odor and/or flavor [14 - 17]. As the identification of fruit volatiles is highly influenced by the extraction and separation procedures applied, as well as by the intrinsic genotype or phenotype-based metabolite differences in fruits of different origin, the data in those studies also differ significantly in quantitative and qualitative aspect. Nevertheless, a number of volatile compounds have been already associated with Cape gooseberry flavor, representing the groups of alcohols, lactones, esters, terpenes, aldehydes, ketones, acids, phenols, *etc.* [16 - 22]. In particular, a study on the aroma compounds of Cape gooseberry fruit from Turkey, completed by liquid- liquid extraction (with dichloromethane as a solvent) and GC-FID/CG-MS separation techniques, indicated 13 components as the potent odor contributors, among which γ-octalactone, γ-hexalactone, ethyl octanoate, 2- heptanone, and nonanal had the highest odor activity values [14].

The identification of the volatile profiles of different plant extracts, as well as their transformation into new products with beneficial activities is equally important for the cosmetic industry, too, as modern societies are currently witnessing an unprecedented demand for natural bioactive products. Regarding Cape gooseberry, the extracts obtained from fruit calyces (INCI name: Physalis Peruviana Calyx Extract; CAS 1620202-03-0) and whole fruit (Physalis Peruviana Fruit Extract) have been listed as cosmetic ingredients (function: skin conditioning) in the referent database of the European Commission [23]. To the best of our knowledge and regarding available references, there have been indeed a very few attempts to investigate *P. peruviana* fruit as a resource for the fragrance and cosmetic industries.

Thus, we hypothesized that Cape gooseberry fruit might also be an advantageous material for processing into an aromatic product (fruit resinoid) with potential use as an active ingredient in cosmetic formulations and/or as a food supplement (flavor enhancer).

Therefore, the main objective of this study was to assess the potential of the resinoid obtained from Cape gooseberry fruit from Bulgaria for use in cosmetics, by revealing its volatile composition and characterizing the rheological and other properties of an author-developed resinoid-enriched cosmetic cream.

2 Materials and methods

2.1 Plant material

The study used fresh Cape gooseberry fruit of the original Bulgarian variety "Plovdiv", kindly provided by one of its creators, Prof. Nikolay Panayotov, Department of Horticulture, Agricultural University, Plovdiv (crop year 2019). For the sake of analysis, the calyces were manually detached and only ripe and undamaged fruit were selected. The gross sample was kept shortly in a refrigerator at 5 - 8°C until processing and analysis.

2.2 Extraction of fruit resinoid and GC-MS analysis

In order to obtain the fruit resinoid, homogenized fresh Cape gooseberry fruit (with moisture content 82.27 ± 0.32%) were extracted consecutively, for 2 h and 2.5 h, respectively, with 95% ethanol at temperature 60°C and solid-to-solvent ratio of 1:8 (w/v). The miscellas from the two extraction stages were combined and then the solvent was completely evaporated on a rotary vacuum evaporator at temperature 40°C. Resinoid yield was determined gravimetrically (Mettler-Toledo precision weight, ± 0.0001 g) and calculated on a dry weight basis (% DW, w/w).

Sample preparation for the GC-MS analysis included additional vacuum-drying of the extracted resinoid (100.0 µL) at 40°C on a centrifugal vacuum concentrator (CentriVap, Labconco, Kansas City, MO, USA). Then 100 µL solution of methoxyamine hydrochloride (20 mg/mL in pyridine) were added and the solution was heated, with constant shaking (300 min^{-1}), for 1 h at 70°C (Thermo Shaker TS-100, Analytik Jena AG, Jena, Germany). The heated solution was cooled and combined with 100 µL of the silylation agent, N,O-bis (trimethylsilyl)trifluoroacetamide (BSTFA).

The resultant sample solution was heated again, at constant shaking (300 min^{-1}, 70°C, 40 min) and injected (1.0 µL volume) into an Agilent 7890A gas chromatograph with a 5975C mass selective detector (Agilent Technologies Inc., Santa Clara, CA, USA). The instrumental unit was equipped with an HP-5ms column (30 m × 0.25 mm, i.d.) coated with poly(dimethylsiloxane) as the stationary phase (film thickness 0.25 µm). Helium was used as the carrier gas, at constant flow rate of 1.0 mL/min; the injector and transfer line temperatures were 250°C; MS source temperature was 230°C; oven temperature was set at 100°C for 2 min, then increased to 180°C at a rate of 15°C/min, held at 180°C for 2 min, and then increased to 300°C at a rate of 5°C/min (held at 300°C for 10 min); total run time was 42 min; the split mode was 20:1; the MS scans covered the range 50 - 550 m/z. Component identification was completed by comparison with mass spectra data libraries [24, own library], based on the respective retention time (RT) and retention (Kovat's) index (RI) values. The latter were calculated using a standard calibration mixture of *n*-alkanes in hexane (C_8 – C_{40}), under the same operational conditions. Compound concentrations were obtained after normalization of the recorded peak areas in the total ion current (TIC) chromatograms and were expressed as percentage of the TIC.

2.3 Preparation of the cosmetic cream

The cosmetic cream (emulsion of the type oil-in-water, O/W) was prepared in the laboratory following a multi-step procedure of emulsion phase combination. First, the individual ingredients of the thermostable phases A and B were weighed on a precision balance, mixed and each of the phases was heated to 80-85°C temperature. Then the two phases were emulsified, by adding phase B (oil phase) to phase A (solvent phase), at constant energetic stirring. The emulsified mass was cooled to 40°C, also at constant stirring. The rest of the phases – phase C (the solubilizer with the fruit extract) and phase D (the thermolabile preservative) – were then consecutively added to the cooled mass. The control sample, not incorporating the fruit resinoid as an ingredient, was prepared following the same steps. The cosmetic ingredients were pharmaceutical or practical grade, respectively, provided by a local supplier of trademarks (trademark disclosure allowance not granted to the authors).

The sensory evaluation of the appearance, color and odor of the cosmetic emulsions was performed by a five-member panel of certified perfumers. Emulsion acidity was registered on a laboratory pH-meter (pH 7110, WTW, Weilheim, Germany). Emulsion stability was determined according to the standard method [25], by centrifugation for 5 min at 6000 min^{-1}, and further confirmed by visual observation within 3 months storage.

2.4 Rheological behavior of the cosmetic cream

The rheological behavior of the prepared cosmetic emulsions was studied on a rotary digital viscometer Brookfield RVDV-II+Pro, equipped with a metal chamber and a cylindrical spindle with a conical head SC4-27 (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA). Preliminary experiments were performed in order to specify the range of shear rates, in which the measurements were possible. The water jacket of the adapter for small samples was connected to an ultra-thermostat (Zeamil Horyzont, Krakow, Poland). During each experiment the chamber was filled with emulsion volume of 10.4 mL, and then heated to 20 ± 0.1°C for a period of 5 min. An experiment was designed, during which the rheological properties of each emulsion were measured at 20 shear rates (D, increasing from 0.1 to 1.02 s^{-1}), as determined by the preliminary experiments. The duration of each cycle was 20 min, in which the spindle rotated at every shear rate for 60 s and at the end the viscometer registered the reading. All of the experiments were performed in triplets.

The resulting data were used for constructing graphical dependencies between the shear stress and the shear rate, which were used to define the rheological properties of the emulsion. The average values of the results from the experiments were fitted by the rheological model of Herschel-Bulkley (1), which had the highest R-squared coefficients. The same file presented the graphical dependencies between the shear rate and the apparent viscosity for the individual emulsions.

$$\tau = \tau_0 + k.D^n \quad (1)$$

where:
τ – shear stress, Pa;
τ_0 – yield stress, Pa;
k – consistency index, $Pa.s^n$;
D – shear rate, s^{-1};
n – flow index.

2.5 Statistical analysis

All analyses were performed in triplicate and the results were presented by the mean value and the corresponding standard deviation (SD). Numerical data were processed using Microsoft Excel 2013 software.

3 Results

According to the objectives of the study, fresh Cape gooseberry fruit were processed by extraction with 95% ethanol in order to obtain a concentrated aromatic product (fruit resinoid) and investigate its potential for use in cosmetics. The principal indicators of the obtained resinoid are presented in Table 1.

Table 1. Principle characteristics of the resinoid from cape gooseberry fruit

Index	Description
Yield, % DW (w/w)	58.78 ± 5.50
Appearance	Viscous mass
Color	Dark orange
Odor	Fruity, with caramel notes and smoke accords

The results from the non-targeted GC-MS analysis of the resinoid are presented in Table 2. Data allowed the identification of 44 individual peaks, corresponding to 98.69% of the total resinoid composition. Eighteen components exceeded 1% content, and five of them were above 3% in the resinoid (major components): 4-o-methyl-myo-inositol (19.04%), glycerol (18.58%), glucose methoxyamine (two isomers, 15.77% and 2.10%), galactose methoxyamine (two isomers, 6.80% and 0.51%), fructose methoxyamine (two isomers, 3.69% and 3.00%), and methylcitric acid (3.38%).

As seen from the data in Table 2, the volatile profile of the obtained Cape gooseberry resinoid was shaped by components representing different chemical classes, and the results from the classification of the identified compounds (equalled to 100%) into groups of chemicals are presented in Fig. 1. The distribution of the components identified by the applied CG-MS sample preparation and analysis procedure showed that resinoid composition was dominated by carbohydrates (65.92% of the identified content) and alcohols (18.83%), followed by organic acids (5.71%), amino acids (5.70%) and fatty acids (3.42%), while the remaining part were minor miscellaneous compounds (hydrocarbons and others).

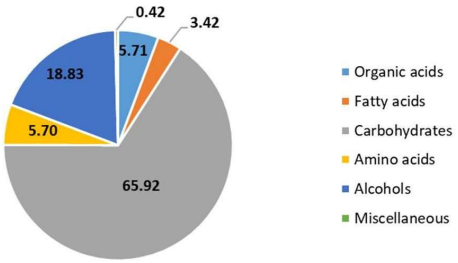

Fig. 1. Chemical profile of the resinoid from cape gooseberry fruit

The high yield, the odor description and the chemical composition of the resinoid supported the feasibility of its incorporation in a finished product. In this study, a cosmetic cream of the type oil-in-water (O/W) emulsion was developed (illustrated in Fig. 2), and its composition is presented in Table 3. No perfume composition was included in the formulation, relying on the odor intensity of the resinoid in the model emulsion.

Some of the descriptors of the cosmetic product are presented in Table 4. As seen from the data, the incorporation of the resinoid affected the sensory properties of the cosmetic cream (color, odor), as well as its pH.

Table 4. Description of the cosmetic cream (O/W emulsion) containing cape gooseberry resinoid

Index	Model emulsion	Control
Appearance	Homogenous fine mass, typical for the type of cosmetic products	
Color	Creamy; yellowish	White
Odor	Specific, with caramel notes/	Odorless
pH, 20 ± 2°C	4.89 ± 0.01[1]	6.24 ± 0.01
Emulsion stability	Stable, without delamination. Homogenous after 3 months	

[1] the data are expressed as the mean value ± SD (n=3)

Fig. 2. Appearance of the formulated cosmetic cream (O/W emulsion):
(1) – control, without cape gooseberry resinoid;
(2) – model formulation, containing cape gooseberry resinoid (photo by authors).

In compliance with study objectives, rheological tests were performed on the developed cosmetic creams (the model and the control samples) and the results were fitted according to the Herschel-Bulkley model (1). Data from those investigations are presented in Table 5.

Table 5. Values of the coefficients[1] in the Herschel-Bulkley model (1)

Sample	k, Pa.s^n	n	τ_0, Pa	R^2
Model emulsion	55.93±0.21[2]	0.67±0.06	7.26±0.14	100
Control	64.19±0.24	0.73±0.03	13.20±0.11	100

[1] τ_0 – yield stress, Pa; k – consistency index, Pa.s^n; s^{-1}; n – flow index; R^2 – coefficient of determination.
[2] The data are expressed as the mean value ± SD (n=3)

As stated earlier, the particular rheological model was chosen on the basis of maximal coefficient of determination values (reaching about 100% in the case of the studied samples), thus accurately describing the flowing of the emulsions. In this rheological model, the fluid behaves like a solid, which begins to flow after the application of a specific stress, denoted as the yield stress (τ_0, Pa). After that threshold, the fluid flows as a pseudoplastic (at n<1) or a dilatant (n>1) fluid.

To facilitate the analysis, the experimental results of the tests before their approximation are presented on Fig. 3 and Fig. 4.

Table 2. Identification of the chemical composition (by GC-MS) of the resinoid from cape gooseberry fruit

No	Component	RT [1]	RI [2]	Content, % of TIC [3]
1	Alanine 2TMS [4]	5.61	1098	0.38 ± 0.0 [5]
2	Oxalic acid 2TMS	5.96	1127	0.14 ± 0.0
3	2-Aminobutyric acid 2TMS	6.21	1162	0.09 ± 0.0
4	Malonic acid 2TMS	6.43	1186	0.17 ± 0.0
5	n-Dodecane	6.72	1200	0.16 ± 0.0
6	Valine 2TMS	6.81	1209	0.12 ± 0.0
7	Glycerol 3TMS	7.36	1278	18.58 ± 0.11
8	Proline 2TMS	7.66	1301	0.32 ± 0.0
9	Succinic acid 2TMS	7.82	1320	0.43 ± 0.0
10	Fumaric acid 2TMS	8.19	1345	0.14 ± 0.0
11	Serine 3TMS	8.45	1376	0.24 ± 0.0
12	Threonine 3TMS	8.62	1392	0.17 ± 0.0
13	Malic acid 3TMS	8.99	1470	0.22 ± 0.0
14	Aspartic acid 3TMS	9.33	1519	0.11 ± 0.0
15	Pyroglutamic acid 2TMS	9.47	1525	0.21 ± 0.0
16	4-Aminobutyric acid 3TMS	9.78	1534	0.36 ± 0.0
17	N-Acetylglutamic acid 2TMS	10.02	1542	0.09 ± 0.0
18	Threonic acid 4TMS	10.33	1567	2.24 ± 0.02
19	2-Ketoglutaric acid methoxyamine 2TMS	10.47	1579	0.19 ± 0.0
20	L-Glutamic acid 3TMS	11.89	1640	1.74 ± 0.01
21	Xylose methoxyamine 4TMS isomer	12.01	1655	0.60 ± 0.0
22	Xylose methoxyamine 4TMS isomer	12.12	1668	2.53 ± 0.01
23	Glycerol-3-phosphate 4TMS	12.98	1773	0.26 ± 0.0
24	Citric acid 4TMS	13.34	1826	0.37 ± 0.0
25	Fructose methoxyamine 5TMS isomer	13.45	1851	3.00 ± 0.02
26	Fructose methoxyamine 5TMS isomer	13.55	1860	3.69 ± 0.02
27	Galactose methoxyamine 6TMS	13.61	1868	6.80 ± 0.06
28	1-Methyl-alpha-D-glucopyranoside 4TMS	13.70	1874	1.15 ± 0.01
29	Galactose methoxyamine 6TMS	13.98	1882	0.51 ± 0.0
30	Glucose methoxyamine 6TMS isomer	14.70	1905	2.10 ± 0.01
31	Glucose methoxyamine 6TMS isomer	14.88	1911	15.77 ± 0.12
32	Hexitol 6TMS	15.37	1920	1.35 ± 0.01
33	Methylcitric acid 4TMS	15.54	1932	3.38 ± 0.02
34	Ascorbic acid 5TMS	15.69	1944	0.12 ± 0.0
35	4-O-Methyl-myo-inositol 5TMS	16.26	1962	19.04 ± 0.17
36	Palmitic acid TMS	17.33	2041	1.07 ± 0.0
37	Stearic acid TMS	18.11	2230	1.87 ± 0.01
38	Melibiose 8TMS isomer	24.34	2455	0.33 ± 0.0
39	n-Docosanoic acid 1TMS	26.41	2649	0.44 ± 0.0
40	Sucrose 8TMS isomer	26.67	2656	1.73 ± 0.01
41	Maltose 8TMS isomer	26.81	2703	2.85 ± 0.01
42	Melibiose 8TMS isomer	26.93	2721	2.69 ± 0.01
43	Sucrose 8TMS isomer	27.15	2742	0.81 ± 0.0
44	Maltose 8TMS isomer	27.66	2790	0.11 ± 0.0

[1] RT – retention time, min; [2] RI – retention index (Kovat's index); [3] TIC – total ion current; [4] nTMS – trimethylsilyl derivate with *n* substituted H-atoms; [5] the data are expressed as the mean value ± SD (n=3)

3 Discussion

Resinoids, representing concentrated (dry) ethanolic extracts obtained from different aromatic plants, are known as traditional fragrance ingredients in perfumery and cosmetics [27], but similar extracts are also common flavorings in foods. In an attempt to widen the range of possible applications of Cape gooseberry fruit and to substantiate their processing into new classes of finished products, the resinoid from the less studied Bulgarian variety of the species was obtained and analyzed. The results (Table 1) indicated very good process efficiency in terms of resinoid yield (58.78% DW), showing that Cape gooseberry fruit had higher resinoid-yielding capacity than many common aromatic plants (8-27%) [27]. Those results were in full compliance with the high yield of another type of aromatic products, a concentrated *n*-hexane extract (4.07%) from the fruit of the same variety achieved in a previous study [28].

Table 3. Formulation of a cosmetic cream (O/W emulsion) containing cape gooseberry resinoid

Phase	Ingredient INCI [1]	Properties	Content, %	
			Model emulsion	Control
A	Aqua	solvent	ad 100	ad 100
	Glycerin	moisturizer	4.00	4.00
B	Glyceryl Stearate (and) PEG-100 Stearate	emulsifier	6.00	6.00
	Glyceryl Stearate	emulsifier	3.00	3.00
	Cetearyl Alcohol	consistency regulator	1.80	1.80
	Cetearyl Ethyl hexanoate	emollient	5.00	5.00
	Paraffinum Liquidum	emollient	6.00	6.00
	Stearic Acid	co-emulsifier; consistency regulator	1.00	1.00
	Caprylic/Capric Triglyceride	emollient	4.00	4.00
	Cera Alba	co-emulsifier; consistency regulator	0.30	0.30
	Methylparaben	preservative	0.20	0.20
	Propylparaben	preservative	0.10	0.10
C	Polysorbate 60	solubilizer	1.00	1.00
	Physalis Peruviana Fruit Extract	active ingredient	1.00	-
D	2-Bromo-2-Nitropropane-1,3-Diol	preservative	0.05	0.05

[1] The names are given according to the INCI [26]

Correspondingly, the high resinoid yield was comparable with that achieved under similar extraction conditions from the fruit of a related *Physalis* species from Bulgaria, *P. alkekengi* L., 47.92 - 58.64% DW [29]. The prospective of Cape gooseberry fruit processing was further supported by the specific olfactory profile with distinguishable odor notes of the obtained resinoid (Table 1).

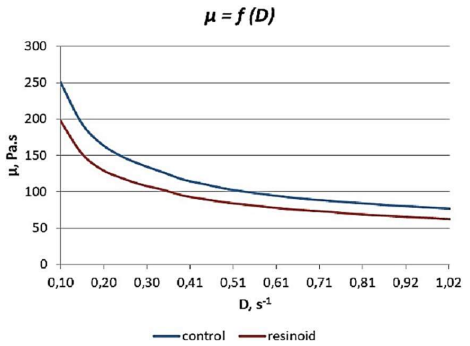

Fig. 3. Graphic dependency between the shear rate (D) and the apparent viscosity (μ) of the cosmetic emulsions.

The study provided, to the best of our knowledge, the first results from the identification of the volatile composition of the extracted fruit resinoid, revealing the presence of different classes of plant metabolites. As seen from the data in Table 2, resinoid composition was not dominated by a few characteristic major components, as in a typical aromatic product, but combined major and minor representatives of various chemical classes. It should be outlined that the identification of predominantly primary plant metabolites (such as carbohydrate derivatives, organic, amino and fatty acids) in the resinoid (Fig. 2) was probably a function of the applied non-targeted GC-MS fractionation and component analysis of the extracted polar phase of Cape gooseberry fruit. For instance, flavonoids previously found to be present in 95% ethanol extracts from whole berries and fruit pulp of the same Cape gooseberry variety (4.65 and 4.58 mg QE/100 g FW, respectively) [9] were not volatile even after derivatization and were not detected in the chromatograms in this study. Those results, however, were in full compliance with previous findings from analysis of other plant extracts under similar identification conditions, for example *Melissa officinalis* [30] or the related *P. alkekengi* species [29], in which hexose sugars, disaccharides, amino acids and organic acids were also the dominant chemical classes.

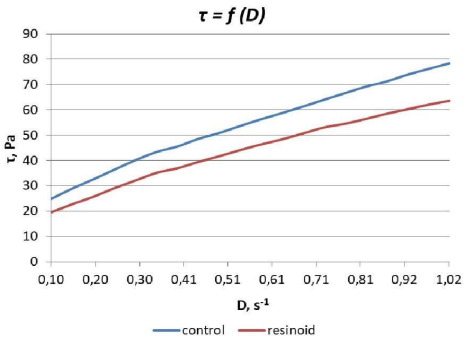

Fig. 4. Graphic dependency between the shear rate (D) and the shear stress (τ) of the cosmetic emulsions.

Reasonably, our results differed from the reported data about Cape gooseberry volatiles obtained under different analytical techniques and regarding other fruit genotypes [14-16, 22], thus opening up opportunities for further research on the volatile profile of the particular Gape gooseberry variety (e.g. terpenoids, carotenoid derivatives, phenolics, *etc.*). The applied analytical procedure did not register the presence of any of the compounds restricted for use in cosmetic products or any of the known human allergens [26].

In order to approve directly the suitability of the obtained fruit resinoid for use in finished products, a cosmetic cream was formulated (Table 3) and prepared (as illustrated on Fig. 2).

The results from the physical and morphological tests of the product (Table 4) showed that the cosmetic cream with 1% fruit resinoid was slightly tinted, yellowish-creamy, and had pleasant gentle caramel-fruity aroma, due to the incorporation of the aromatic product. In view of the results from the chemical analysis, it had been anticipated that the addition of Cape gooseberry resinoid would increase the acidity of the product, so the composition of the control preparation (without the resinoid) was designed in a way that would guarantee the applicability of the cosmetic cream. The addition of the active ingredient indeed lowered considerably cream pH (4.89 in the model emulsion vs. 6.24 in the control), but the value achieved for the final product successfully matched the acceptable range of pH for topically applied products for daily use (4.0-5.5). The cream remained homogenous in the emulsion stability test, suggesting solid bonding of the base ingredients, as well as of the added resinoid.

The rheological behavior of cosmetic emulsions (creams, lotions, *etc.*) is an important aspect in the quality assessment of that type of cosmetic products, as it affects the mode of their application on the skin, the consumer perception and the safe product storage. Therefore, at the next step of the study the rheological characteristics of the control and the model creams were analyzed. The graphical dependencies presented in Fig. 3 clearly showed the negative correlation between the shear rate and the apparent viscosity of the products. Such behavior is characteristic of pseudoplastic non- Newtonian fluids. A distinctive feature of such fluids is the slow degradation of the molecular bonds that make up the emulsion with the increase of shear rate, which leads to a corresponding decrease in fluid viscosity. The control sample had a significantly higher viscosity compared to the sample containing fruit resinoid; by more than 22% in the range of lower shear rate values, and by 19% at the end of the studied shear rate interval. Fig. 4 revealed the nonlinear nature of the correlation between the shear rate and the shear stress of the cosmetic emulsions, which confirmed the assumption that the two studied emulsions flew as non-Newtonian fluids. In both cases, in order to initiate a leak, it is necessary to apply a yield stress (τ_0, Pa) (Table 5), after which a positive correlation between the shear rate and the shear stress could be observed. Such behavior is typical for the Herschel-Bulkley fluids. It can be seen that the control sample registered higher values of the shear stress, by more than 20%, in comparison with the model cream sample containing the resinoid (Fig. 4). The flow index *n* in the Herschel-Bulkley model (1) took values less than 1.00 in both cases (Table 5), which indicates that once the initial yield stress is applied and the emulsions begin to flow, they behave like pseudoplastic fluids. It could be assumed that such pseudoplastic behavior would facilitate the good skin coverage by the cosmetic cream in its typical energetic topical application.

5 Conclusions

The study presents first results from the investigation of a concentrated aromatic product (the fruit resinoid) obtained by extraction of the fruit of *P. peruviana* L. (Cape gooseberry) cultivated in Bulgaria. It provides new data about resinoid chemical composition (by GC- MS) and organoleptic characteristics. The registered high yield, the identified volatile composition and the specific olfactory profile of the resinoid substantiated its inclusion as an active ingredient in a model formulation of a cosmetic product (skin-care cream), further assessed in terms of sensory and rheological properties. The results revealed that the studied cosmetic emulsions had the rheological behavior of pseudoplastic non- Newtonian fluids and that resinoid inclusion reduced cream viscosity. Based on the achievements of the study, it could be concluded that the resinoid from Cape gooseberry fruit has the potential to be a reasonable candidate as an active ingredient in cosmetic preparations. Of course, further research is definitely needed in order to reveal the complex effects of Cape gooseberry resinoid addition, such as those related to its antioxidant, antimicrobial and other beneficial properties, which would be the focus of future investigation.

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