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The effect of selected supercritical CO_2 plant extract addition on user properties of shower gels

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The formulations of washing cosmetics i.e. shower gels, containing extracts obtained during supercritical CO_2 extraction process as active ingredient, were developed. The subject of the study was the analysis of the physico-chemical and user properties of the obtained products. In the work supercritical CO_2 extracts of black currant seeds, strawberry seeds, hop cones and mint leafs were used. The formulation contains a mixture of surfactants (disodium cocoamphodiacetate, disodium laureth sulfosuccinate, cocoamide DEA, cocoamidepropyl betaine, Sodium Laureth Sulfate). Various thickener agents were applied to the obtained desired rheological properties of the cosmetics. Among others, sorbitol acetal derivatives, methylhydroxypropylcellulose and C10-30 alkyl acrylate crosspolymer were used. For stable products, the effect of extracts addition (black currants seeds, strawberries seeds, mint and hops, obtained from supercritical CO_2 extraction process) on the cosmetics properties, such as pH, viscosity, detergency and foam ability, were determined. The obtained results showed that the extracts could be used as components of shower gels.

Keywords: supercritical CO_2 extract, black currant seeds, strawberry seeds, hop cones, mint leafs, shower gel.

INTRODUCTION

The cosmetics containing natural ingredients are very popular. This situation forces the cosmetic industry to search for new recipes. In the case of shower gels, preferred cosmetics contain mild surfactants, especially natural ingredients having beneficial effect on the condition of skin and hair, and rheology modifiers that effect on the ease application of the cosmetics.

The method of obtaining plant extracts is important for their quality and the possibility of their use in cosmetics. The method of particular significance among others is obtaining these extracts in supercritical CO_2 conditions. Supercritical fluid extraction technique takes many advantages in comparison with traditional methods of extraction. The process is highly efficient and the obtained extracts do not contain residues of conventional organic solvents. Additionally, supercritical CO_2 extractions are carried out at relatively low temperatures (10–70°C) in oxygen-free atmosphere what avoids thermal and oxidative degradation of the bioactive components in the extract. Furthermore, supercritical CO_2 extraction is an environment-friendly process[1–3].

The extracts of special interest, due to their biological properties, which may be used in cosmetics like shower gels, are the extracts of black currant seeds, strawberry seeds, hop cones and a mint leaves.

The black currant seeds extract and strawberry seeds extract are a source of triglycerides and biologically active ingredients. They contain significant amounts of γ-tocopherol, they are natural sources of α-linolenic acid[4, 5].

The oil of black currant seeds belongs to the group of oils which are the richest in γ-linolenic acid (GLA). Furthermore, it contains also α-linolenic acid (ALA) and stearidonic acid. The black currant seeds oil stands out from the other oils because such a combination of fatty acids is not found in any other oil[6]. Black currant seeds oil is used to treat a number of skin diseases (atopic dermatitis, eczema, psoriasis and juvenile acne). It prevents breaking nails and hair loss. It is used in cosmetic formulations designated for dry, mature and mixed and acne skin[7].

The extract from hop cones shows astringent, bacteriostatic, bactericidal and antiseptic properties[8, 9]. It exhibits antiradical properties due to the high content of quercetin.

In hair cosmetics hop extract is used because of its anti-fungal and antiseborrhoeic properties[10]. The active substances contained in hop cones, reduce brittleness of the hair, nourish the hair giving them shine, woolliness; moreover it strengthens hair and prevents hair loss or dandruff formation[11–13]. In cosmetics hop extract is most commonly used in bath liquids, shower gels, creams and regenerative masks[14–16].

The mint leaves extract contains essential oil (source of menthol and menthone), tannins and flavonoids[17]. As a result, it exhibits an antiseptic, anti-inflammatory, antimicrobial, antibacterial and antifungal activity[18]. In cosmetics industry mint extract is used as an active agent in shampoos, balsams and perfumes[19–21].

In the developed formulations of shower gels, extracts of black currant seeds and strawberry seeds are used to impact specific properties which are characteristic of normal hair cosmetics. However, the formulations containing the extract of hop cones and mint leaves have the properties suitable for the oily and dandruff hair. All the extracts used for such cosmetics have a beneficial effect on the skin, relieving its irritation and acting as an antibacterial and antifungal factor.

EXPERIMENTAL

As a result of preliminary tests, concentrations of surfactant used in shower gels were determined. The usefulness of different natural thickeners were also examined. Among others, sorbitol acetal derivatives as a dibenzylidene sorbitol (1,3:2,4-Di-O-benzylidene-D-sorbitol), cellulose derivatives as a methylhydroxypropylcellulose and acrylates (C10-30 alkyl acrylate crosspolymer)

were studied. On the basis of the obtained results, the ingredients used in the final formulations were selected.

In this study supercritical CO_2 extracts of black currant seeds, strawberry seeds, hop cones and mint leaves were used. The extracts were produced by Instytut Nowych Syntez Chemicznych w Puławach. The producers of the other ingredients are provided at Table 1. A mixture of disodium cocoamphodiacetate, disodium laureth sulfosuccinate, cocoamide DEA, cocoamidepropyl betaine, sodium laureth sulfate (as surfactants), acrylates (as a viscosity modifier), sodium benzoate (as a preservative), citric acid (as an acidity modifier) were used in our compositions (Table 2). In cosmetic formulations thickened by the polyacrylic acid derivatives triethanolamine was used as a pH regulator.

The procedure of formulations preparing.

As a result of tests carried out, it was found that in order to set up properties of the formulation it is necessary to combine the ingredients in the following order: a rheology modifier should be introduced, under intensive stirring, into water, having a certain amount in the formulation. The process should be conducted, at the temperature ranging from 30 to 50°C, until complete dispersion of the component.

Then the triethanolamine should be added and mixed until the gel is completely transparent. After heating the gel to the temperature of 70 to 80°C under continuous stirring cocoamide DEA should be added and then mixing should be continued until a homogeneous white gel is obtained. The disodium cocoamphodiacetate and disodium laureth sulfosuccinate should be combined together at about 50°C and then the extract must be added in the amount specified in the recipe. It is necessary to mix the whole until the complete dispersion of the extract. The cocoamidepropyl betaine and sodium laureth sulfate must be added into the obtained homogeneous mixture.

Mixing should be continued until the mixture is homogeneous. Then the surfactant mixture containing the extract should be placed into the prepared gel. The whole mixture should be intensively stirred for about 30 minutes and simultaneously cooled to the temperature of about 30°C. The merger of the components is followed by the loss of the mixture viscosity. The mixture should be put away for an hour and then the citric acid should be added until the pH of the solution reaches the range of 5.5 to 6. After the pH of the mixture is stabilised, the formulation again returns to the form of a gel.

Formulations were prepared with the use of IKA magnetic stirrer with the temperature and the speed of rotation controlled.

The pH measurement was carried out using the pH--meter Mettler Seven Multi Toledo equipped with a glass electrode Inlab 410.

The rheological properties of the obtained and stable shower gels were studied with the use of Brookfield Rheometer Model R/S-plus, equipped with a cone-plate type measuring system (cone C75-1), at a room temperature (25°C), with variable viscosity shear rate in the range of values from 1 to 500 s^{-1}. The measurement was repeated three times for each formulation.

The surface tension of 1% aqueous solutions of the obtained formulations was measured with STA-1A tensiometer, equipped with CCNR Ministat 125 thermostat, at T = 25°C. For each sample, the mean value was calculated on the basis of 7 measurements.

The foaming properties test was performed by the Ross-Miles method based on the measurement of the volume of the foam produced by the free flow of the tested solution onto the surface of the same solution contained in the cylinder, according to the Polish Standard PN-ISO 696:1994[22].

The ability of foam is defined as the volume of foam produced in the measurement conditions. The

Table 1. The producers of components used

Ingredients	INCI name	Producer
Rewoteric AMC	Disodium cocoamphodiacetate	Evonik Industries AG
Rewopol SB FA 30B	Disodium laureth sulfosuccinate	Evonik Industries AG
Rewomid DC 212S	Cocoamide DEA	Evonik Industries AG
Tego Betain F50	Cocoamidepropyl betaine	Evonik Industries AG
Sulforokanol L270/1	Sodium Laureth Sulfate	PCC Rokita S.A.
Carbopol Ultrez 21 Polymer	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	Lubrizol Advanced Materials, Inc.
Triethanolamine pure	Triethanolamine	POCh S.A.
Sodium benzoate	Sodium benzoate	Brenntag Polska Sp. z o.o.
Citric acid	Citric acid	Sigma-Aldrich

Table 2. The composition of the examined formulations

Ingredient (INCI name)	VMI701 mint leaves [wt%]	VTR701 strawberry seeds [wt%]	VCH701 hop cones [wt%]	VCP701 black currant seeds [wt%]
Disodium cocoamphodiacetate	7.67	8.18	9.01	9.30
Disodium laureth sulfosuccinate	9.26	9.49	10.47	11.00
Cocoamide DEA	3.41	3.15	2.61	2.35
Cocoamidepropyl betaine	10.52	13.37	14.23	14.09
Sodium Laureth Sulfate	5.35	5.31	5.84	6.15
supercritical CO_2 extract	0.59	0.57	0.52	0.67
Acrylates/C10-30 alkyl acrylate crosspolymer	0.23	0.22	0.23	0.22
Triethanolamine	0.23	0.24	0.22	0.22
Sodium benzoate /preservative/	qs.	qs.	qs.	qs.
Citric acid	qs.	qs.	qs.	qs.
Aqua	62.73	59.47	56.86	55.99
Sum	100.00	100.00	100.00	100.00

foam stability (Sp) were calculated with the formula: $Sp = (V_5/V_0) \cdot 100\%$ where V_0 – it is the volume of the foam produced after 30 seconds from the end of the outflow solution from the reservoir, V_5 – foam volume after 5 minutes from the end of the outflow solution from the reservoir.

RESULTS AND DISCUSSION

The formulations characterized by the stability during 30 days, at the room temperature, were selected for the measurement of their properties. During this time there were no delamination in the gel structure. The formulations characterized by a bright color. The formulation containing strawberry seeds extract was cream-colored, black currant seeds extract was straw-colored, while the others extracts are yellow-green.

Not all of the formulations are completely transparent after venting. The scent of formulations containing extracts of mint leaves, strawberry seeds and black currant seeds is delicate and characteristic of the extract used. In the case of hop cones extract the odour of obtained product is intensive, but is not irritating with the concentrations used. The consistency of formulations was homogeneous. They were easy to distribute on the skin and slowly rinsed with running water. The final pH value of the formulations (5.5–6.0) is within the acceptable pH level for formulations intended for washing hair and skin (4.5–8.0).

Rheological properties

In the case of cosmetic products, rheological properties play an important role. They are important for defining and controlling the characteristics of the product such as stability, consistency, an easy flow-out of the packaging, and an easy application on the skin. In the case of shower gels, rheological properties have also an effect on the retention of the formulation on the skin in the presence of a water stream and the dilution time of the detergent. Figure 1 shows the viscosity curves of the obtained formulations.

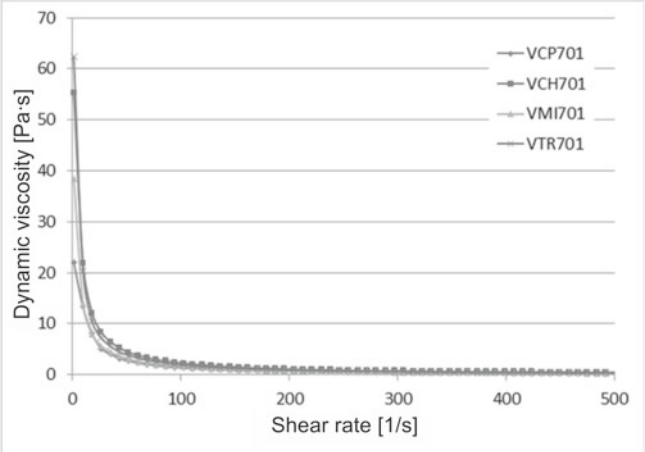

Figure 1. Viscosity curves of shower gels containing supercritical CO_2 extracts. Shower gel: VCH701 – hop cones, VCP701 – black currant seeds, VMI701 – mint leaves, VTR701 – strawberry seeds

All the shower gels are non-Newtonian liquids with pseudoplastic rheological behaviour. Moreover, it was evidenced that there was no significant influence of the extract addition on the rheological properties of the obtained formulations.

All the formulations showed satisfactory rheological properties. The lack of evident differences within this property of particular formulation indicates a well-chosen base surfactants and little influence of the type of the extract used on the final product properties.

Measurement of surface tension

Table 3 showes the obtained results. It follows that all the studied formulations are characterized by similar values of surface tension. This is understandable because the cleaning properties of the washing cosmetics compositions particularly depend on the contents of surface-active compounds used in the recipes. In the case of the prepared shower gels the same kind and concentration of detergents were applied. The addition of the extracts has not significant influence on the surface tension of studied gels.

Table 3. The surface tension of 1% aqueous solusions of the obtained shower gels

Name of gels	VMI701 mint leaves	VTR701 strawberry seeds	VCH701 hop cones	VCP701 black currant seeds
Average surface tension [mN/m]	25.57	24.36	24.43	25.20
Standard deviation	±0.04	±0.03	±0.06	±0.04

The foaming properties

The volume and foam stability of 1% aqueous solutions of gels was studied in distilled water and in the hard water. The test was carried out also in the solutions which contained castor oil as a sebum, in a 1:1 ratio with the tested gel. The obtained results are shown in Table 4.

The obtained results show that all the formulations are characterised by good and comparable foaming properties. Moreover, the foam stability is comparable too, in all the cases – in distilled water, in hard water and in presence of sebum. Additionally, the kind of the extract used does not influence the foam-forming ability of the shower gels.

CONCLUSIONS

The obtained formulations are characterized by high stability of user properties which evidences well-chosen base surfactants and rheology modifier.

The obtained results showed that plant extracts, obtained with supercritical CO_2 extraction process, could be used as a component of shower gels compositions. The addition of extracts does not have any significant effect on the surface tension, foam ability and viscosity of the studied gels. Despite the differences in the composition of the extracts, there were no differences in rheological and foaming properties of the gels.

The extracts from the black currants seeds, strawberries seeds, mint and hops, obtained with supercritical CO_2 extraction process, are the sources of biologically active ingredients. Their addition into washing formulation improves the skin conditioning properties of the products.

Table 4. The foaming properties of obtained formulations

		VMI701 mint leaf	VTR701 strawberry seeds	VCH701 hop cone	VCP701 black currant seeds
Distilled water	V_0 [cm^3]	264.2	251.0	224.6	211.4
	V_5 [cm^3]	237.8	237.8	198.2	184.9
	S_p [%]	90.0	94.7	88.2	87.5
Hard water	V_0 [cm^3]	264.2	264.2	237.8	290.6
	V_5 [cm^3]	237.8	237.8	224.6	251.0
	S_p [%]	90.0	90.0	94.4	86.3
Hard water with the addition of castor oil	V_0 [cm^3]	290.6	287.9	290.6	290.6
	V_5 [cm^3]	264.2	264.2	264.2	264.2
	S_p [%]	90.9	91.7	90.9	90.9

The prepared formulations can provide products for companies involved in the production of the cosmetics of shower gel type.

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