BIOLOGICALLY ACTIVE PROPERTIES OF PLANT EXTRACTS IN COSMETIC EMULSIONS

Ruslana Harhaun[a], Oleksandra Kunik[a*], Diana Saribekova[a], Giuseppe Lazzara[b]

[a] Kherson National Technical University, Kherson, Ukraine, 73008, st. Beryslavskoe shose, 24.

e-mail:
Ruslana Harhaun - rusiaharhaun@gmail.com
Oleksandra Kunik - kulish.aleksa@gmail.com
Diana Saribekova - <dina15box@gmail.com>

[b] University of Palermo, Palermo, Italy, 90133, Piazza Marina, 61.

e-mail: <giuseppe.lazzara@unipa.it>

[*] Corresponding author: Ruslana Harhaun - rusiaharhaun@gmail.com

Abstract

Describes biologically active properties aquatic plant extracts of domestic herbaceous species as a part cosmetic emulsion in this article. In particular, the antioxidant features related to vitamins, flavonoids, coloring, extractive and tannins were reported. The following research methods as qualitative analysis on groups of biologically active substances, thin-layer chromatography, titrimetry and photometry were used in the work. The ability of extracts to influence the physico-chemical, organoleptic and antioxidant properties of cosmetic emulsion samples was established. The ability of the extracts to exhibit antioxidant and prooxidant effects in cosmetic emulsion samples was determined. This article represents a contribute in the identification of plant extracts and their use as biologically active additives in cosmetic emulsion.

Keywords: plant extracts, polyphenols, biologically active substances, antioxidant activity, cosmetic emulsion.

1. Introduction

The development of synthetic strategies allowed expanding the raw material base for the manufacture of cosmetic products by creating customized substances that are used as additives contributing to a significant expansion of the range of cosmetics. Nevertheless, the use of cosmetics from natural basis is still attractive for consumers and therefore for producers.

Today, cosmetic companies are focused on new technologies and explore alternative sources of raw materials, especially of plant origin, because they are of high biological value and environmental friendly. The value of plant material determined by the content of biologically active substances, the synergy of their action and the high degree of assimilation by the human body make the plant extracts a valuable source of active substances.

Recently, the application of natural triglycerides for lipase-catalyzed esterification of structurally diverse flavonoids – esculin, naringin and phloridzin was reported[1]. Furthermore, esculin ester mixtures were

incorporated in gel emulsions, and their effects on trans-epidermal water loss (TEWL) as well as skin sensitivity was examined. The obtained results have shown significant effect for all examined preparations containing oil-derived esculin esters, making them very prospective for applications in skin care products.

Considering the wide raw material base, the study of biologically active substances of plant origin is involved in a significant number of scientific works, spanning to the protection of human health to a more simple cosmetic action. For example, natural antioxidants were proposed to inhibit various diseases, such as Alzheimer's[2], cancer[3,4]. Recent findings report on plant extracts that have a high content of polyphenols, which result in strong antioxidant properties, and in turn, they can positively affect the human body in the treatment of cancer and can be used to treat neurodegenerative diseases[1,3]. Vegetable raw material is a promising composite for the pharmaceutical[5,6], cosmetic industry[7], but also for food industry[8-10]. Dietary and nutritional supplements based on herbal extracts are among the most popular[11]. The main problem of their production are connected with the standardization and certification of products and the lack of a universal methodology for analyzing the quality and composition of active ingredients. Recent findings describe the methods of sample preparation and analysis that can be used to determine the biologically active substances in food additives based on plant extracts and to assess the purity of plant extracts in these preparations.

The trends of the cosmetic industry require the use of components of plant origin that have polyfunctional properties and long-lasting directional effect. One of the methods for solving this problem is the microencapsulation of biologically active substances[12]. The findings obtained show the significant benefits of using microencapsulation for the storage and controlled release of biologically active substances in cosmetic compositions.

The use of natural plant raw materials in cosmetic compositions necessitates the use of preservatives. This raises the problem of quickly determining their content and identification in complex compositions. Recently, a new method for the analysis of benzylparaben in cosmetics has been reported[13]. The

methodology developed gives a simple and economical way to determine the preservative, high selectivity, easy reproducibility. This makes it possible to use this method for routine monitoring of benzylparaben in cosmetics.

Industries such as food, mineral, chemical, pharmaceutical and cosmetic, in addition to the latest production technologies, are trying to improve waste treatment and wastewater treatment technologies[14]. Application of eco-friendly plant-based bioflocculants in wastewater treatment has attracted significant attention lately with high removal capability in terms of solids, turbidity, color, and dye. However, moderate flocculating property and short shelf life restrict their development. To enhance the flocculating ability, natural polysaccharides derived from plants are chemically modified by inclusion of synthetic, nonbiodegradable monomers (e.g., acrylamide) onto their backbone to produce grafted bioflocculants. A theoretical justification for the efficiency of using plant raw materials as wastewater bioflocculants, processing methods, and flocculation mechanism was reported[14].

For optimal use of plant extracts, it is necessary to consider parameters such as the dosage, the period of administration, monitoring the impact of related components that can block the action of additives.

In this work we focused on the application of plant extracts as biologically active components for cosmetic formulations. The advantage of natural plant extracts is that they contain hundreds of components that in the complex can have a significant effect on the functions and properties of the cosmetic emulsion.

Given the growing conditions of raw materials and production technology, extracts can vary both in qualitative and in the quantitative composition. Thus, the quality of the different bioactive substances and their contents may differently effect the properties of final products. Therefore, a comprehensive study of the effect of the ratio of biologically active substances from extracts on the properties of the cosmetic product is needed. The use of complex plant extracts will improve the protocol for the formulation of the cosmetic products by replacing a number of individual synthetic active components with the natural biological complex possessed by the extracts.

We aimed at determining the qualitative and quantitative composition of biologically active sub-stances from plant extracts of domestic production, and their antioxidant properties in cosmetic emulsions with a special focus on synergistic effects.

2. Material and methods

Aquatic plant extracts of domestic production from herbaceous plants: calendula (Calendula Officialis L.), lavender (Lavandula vera DC), wormwood (Artemisia Absinthium L.) and lilac (Syringa Vulgaris L.) were used.

The group of water-soluble vitamins (B_1, B_2, B_3, B_5, B_6, P, C) in the investigated extracts was determined by qualitative analysis[15]. Quantitative content of vitamin C in plant extracts was determined by the iodometric method[16]. Identification of qualitative composition of flavonoids was determined by thin-layer liquid chromatography[17] and a number of qualitative reactions.

Quantitative content of flavonoids in extracts was determined by spectrophotometric method. Select 4 ml of the test extract (solution A), place in a 25 ml volumetric flask, add 2 ml of a 2% alcohol solution of aluminum chloride and bring the volume to the mark with 95% alcohol. After 20 min., measure the optical density on a spectrophotometer at a wavelength of 410 nm in a cell with a layer thickness of 10 mm. Prepared solution B is used as the comparison solution. To prepare solution B: 4 ml of solution A is taken, placed in a 25 ml volumetric flask, 1 – 2 drops of dilute hydrochloric acid are added and the solution volume is adjusted to 95% with alcohol. The content of flavonoids in terms of avicularin and absolutely dry raw material in percent (X) is calculated by the formula:

$$X = (D \cdot 25 \cdot 100) / (330 \cdot m) \quad (2.1)$$

D – the optical density of the test extract;

330 – specific absorption rate of avicularin complex with aluminum chloride at 410 nm;

m – weight of sample in grams;

The content of colorants was carried out using photometric method for the standard solution of cobalt

sulfate ($CoSO_4 \cdot H_2O$). In this method it is conventionally accepted that 1 L of an aqueous solution containing 20 g of crystalline cobalt is equivalent in color to an anthocyanin dye solution with a concentration of 22 mg of a dye substance (enin) in 1 L. Pipette 1 ml of the analyzed extract, quantitatively transfer into a volumetric flask per 100 ml, the contents of the flask is brought with distilled water to the mark. Then remove from the flask 10 ml of the resulting solution, transfer to a volumetric flask of 100 ml, add 5 ml of concentrated hydrochloric acid, bring the contents to the mark with distilled water and stir. The resulting solution is placed in a cell with a layer thickness of 10 mm and measure the optical density on the photocolorimeter at a wavelength of 540 nm. The content of colored substances in the extract is calculated by the formula:

$$X = (0{,}022 \cdot D_2 \cdot 1000) / (m \cdot D_1) \quad (2.2)$$

X – the concentration of the dyes in the extract, g/L;

D_1 – the optical density of a standard solution of cobalt sulfur at a wavelength of 540 nm;

D_2 – the optical density of the extract at a wavelength of 540 nm;

m – the mass of the sample extract, g;

0.022 – the concentration of enine equal to 0.022 g in 1 liter of standard solution.

The content of tannins was determined by titrimetric methods. For carrying out the experiment, select 2 ml of the finished extract, place in a conical flask with a capacity of 100 ml, add 60 ml of distilled water and 2 ml of indigosulfonic acid solution and titrate with constant stirring of 0.1 mol/L potassium permanganate solution to a golden yellow color. In parallel conduct a control experiment, titrating 2 ml of indigosulfonic acid in 60 ml of distilled water. 1 ml of 0.1 mol/L potassium permanganate solution corresponds to 0.004157 g of tannins in terms of tannin. The content of tannins is determined in percentage (X) by the formula:

$$X = (V_1 - V_2) \cdot K \cdot D \cdot V \cdot 100 / m \cdot V_3 \quad (2.3)$$

V_1 – the volume of potassium permanganate that has gone to titration, ml;

V_2 – volume of potassium permanganate for titration of control solution, ml;

K – correction for the titer (oxalic acid);

D – conversion factor for tannin (for hydrolyzed - 0,004157; condensed tannins - 0,00582);

V – total volume of the extract, ml;

m – weight of raw material, g;

V_3 – volume of extract taken for titration, 10 ml.

The content of extractives was determined by thermos-gravimetric methods. For the test pipette, select 25 ml of the finished test extract and transferred to a previously dried at a temperature of 100 – 105°C to constant weight and accurately weighed porcelain cup with a diameter of 7 – 9 cm and evaporated in a water bath to dryness. The cup with the residue is dried at a temperature of 100 – 105°C to constant weight, then cooled for 30 min. in a desiccator, at the bottom of which is anhydrous calcium chloride, and weighed. The content of extractives in percent (X) in terms of absolutely dry substance is calculated by the formula:

$$X = (m \cdot 100\%) / (m_1 \cdot (100 - W)) \quad (2.4)$$

m – the mass of dry residue after drying, g;

m_1 – the weight of the sample extract before drying, g;

W – weight loss when drying the sample extract, %.

The antioxidant activity of the extracts and samples of the cosmetic emulsion with the addition of extracts was determined by the Oyaizu method (FRAP method)[18] and by the ability of antioxidants to inhibit the auto-oxidation of adrenaline in vitro. To 4 ml of 0.2 M sodium carbonate buffer, pH = 10.65, 0.2 ml of 0.1% pharmacy solution of adrenaline hydrochloride was added, stirred thoroughly and quickly, placed in a spectrophotometer and the optical density was determined after 30 sec. for 10 min. at a wavelength of 347 nm in a cell with a layer thickness of 10 mm on a spectrophotometer "SPECOL II". Then 0.06 ml of the test solution of the extract and 0.2 ml of 0.1% solution of adrenaline hydrochloride were added to 4 ml of buffer, stirred and the optical density of the solution was measured. To account for the effect of the intrinsic color of the extracts, a buffer solution with an adrenaline-free extract was

used as a control sample. Antioxidant activity is expressed as a percentage inhibition of adrenaline auto-oxidation and is calculated by the formula:

$$AA,\% = (D_1 - D_2) \cdot 100 / D_1 \quad (2.5)$$

D_1 – the optical density of the adrenaline hydrochloride solution added to the sodium carbonate buffer;

D_2 – the optical density of the test extract and adrenaline hydrochloride added to the sodium carbonate buffer.

As an inert basis for the study of the properties of plant extracts was developed cosmetic emulsion used with the following component composition, %: mineral oil – 25, emulsifier (Eumulgin prisma) – 0.35, co-emulsifier (cetearyl alcohol) – 4, preservative (methyl ether para-hydroxybenzoic acid) – 0.5, distilled water – up to 100.

Organoleptic (appearance, color, odor), physical and chemical properties (colloidal and thermal stability, pH) samples of cosmetic emulsion were determined according to literature[19-21].

3. Results and Discussion

The presence of certain groups of vitamins, their identification in aqueous plant extracts by qualitative reactions was proved. The results of qualitative analysis (table A.1**.** Supplementary material) indicate the presence in the extracts of vitamins such as: B_1, B_3, B_5, B_6, P, C.

Negative reaction to vitamin B_2 can be explained by its ability to very slightly soluble in water (only 0.012% at 25°C), even less in alcohol, butanol, chloroform. Since the investigated extracts are from water, the presence of vitamin B_2 is unlikely.

Lack of vitamin B_6 can explained by the fact that it is inherently pro-vitamin, vitamin properties are manifested directly in the body in converting to pyridoxal.

Chromatographic analysis of the qualitative composition of flavonoids presented in Table 3.1.

Table 3.1. Value of coefficients Rf for plant extracts in the system of eluents n-butanol – glacial acetic acid – water (6: 1: 2)

Value of the coefficient of mobility, (Rf)	Plant extract			
	calendula	lavender	wormwood	lilac
	0.856	0.846	0.834	0.853

The chromatographic spectrum of the spots of polyphenols in the extracts, clearly evidenced that the greater part is flavonoid, derivatives of flavones, flavanones, flavanols, flavanonols and halconies. Such results confirm qualitative reactions and displays of chromatograms under UV. Flavanols and their glycosides, as a rule, have yellow-green stains, and flavones and flavanones are brownish-green, dark. It should be noted that in extracts of calendula, lavender and wormwood the predominant content is from flavanols derivatives, but in the extract of lilac – flavones and flavanones.

The values of the coefficients of Rf of calendula and lilac extracts indicate their approximate composition of flavanoid derivatives of flavanone derivatives (5,6,7-trioxiflavanone, 3′,4′,5,7-tetraoxiflavanone), flavone (3,4′-dimethoxiflavone, 4′,5,7-trioxiflavone), flavanole (3′,4′-dioxiflavanole), flavanonole (3′,5,7-trioxiflavanonole, 3′,4′,5,7-tetraoxiflavanonole), chalkone (2,3,4-trioxichalcone, 2,3,3,4,4-tetroxichalcone). The values of Rf indices of lavender extracts and the bitter wormwood make it possible to assume the presence of flavanone derivatives (5,6,7-trioxiflavanone, 3′,4′,5,7-tetraoxiflavanone), flavone (3,4′-dimetoxiflavone), flavanole (3,3,4-dioxiflavanole), chalkone (2,3,4-trioxichalcone)[17].

Quantitative content of coloring substances, vitamin C, flavonoids, tannins and extractives are presented in Table 3.2.

Table 3.2. Quantitative content of biologically active substances in investigated extracts

№	Indicator	Plant extract			
		calendula	lavender	wormwood	lilac
1	Coloring substances, g/l	266.77	269.74	292.97	1440.87
2	Vitamin C, g/l	13.20	11.00	8.80	59.40
3	Sum of flavonoids, %	5.09	3.10	0.61	3.62
4	Tannins, %	0.73	2.89	1.45	2.59
5	Extractive substances, %	0.10	0.08	0.10	0.30

The obtained data (Table 3.2) show that the content of biologically active substances in plant extracts is

highly dependent on the plant. So, lilac extract has the highest content of vitamin C, coloring and extractive substances; calendula extract is high in the amount of flavonoids; the extracts of the wormwood and lavender are similar to the content of biologically active substances and occupy an intermediate position.

Since extracts have a very complex chemical composition, for an effective practical use as antioxidant additive a quantitative assessment of their antioxidant activity is mandatory. In addition, when evaluating antioxidant capacity, it is necessary to consider not only the nature and content of reducing agents in the investigated mixture, but also the possibility of their mutual influence (such as synergism or antagonism). The kinetics of inhibition of the cation of the radical has a fast and slow phase therefore it allows to determine the activity of fast and slow-reducing antioxidants. In order to study the primary, fast-reducing antioxidant properties of plant extracts (the ability to inactivate directly free radicals of oxygen, eliminating their effect), the FRAP method was used to estimate a wider range of antioxidants, including antioxidants with low oxidative-reduction potential (Figure 3.1).

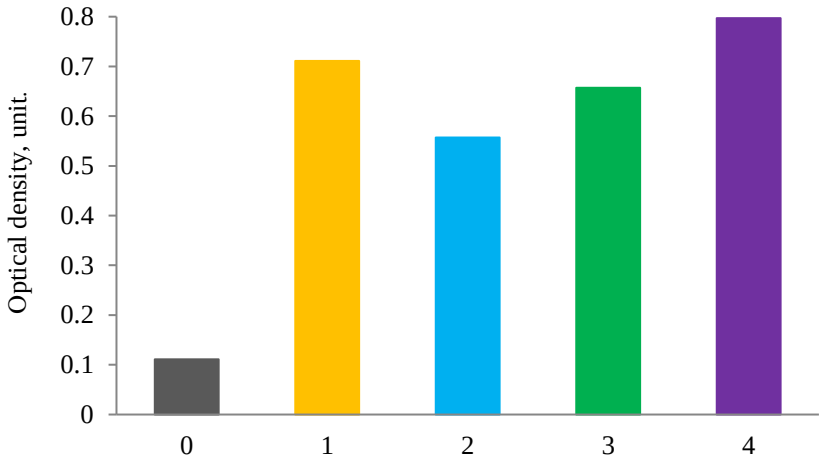

Figure 3.1. Antioxidant activity of plant extracts, determined by FRAP method: 0 – solution of comparison, 1 – extract of calendula, 2 – extract of lavender, 3 – extract of wormwood, 4 – extract of lilac.

The analysis of the FRAP results (Figure 3.1) shows that the plant extracts have high antioxidant proper-

ties. It should be noted that extracts of calendula and lilac have the highest oxidative-reduction potential due to the complex of biologically active substances.

In order to determine the state of antioxidant protection of the organism itself under conditions of pathological processes, the activity of the superoxide dismutase enzyme (SOD) was investigated. This enzyme catalyzes the conversion of the highly reactive anion of the oxygen radical (O_2^-) into the less active hydrogen peroxide and molecular oxygen by means of equation 3.1:

$$O_2^- + O_2^- + 2H+ = H_2O_2 + O_2 \quad (3.1)$$

The literature describes a large number of methods for determining SOD[17]. One of the widely used method is based on the ability of the enzyme to inhibit the auto-oxidation of adrenaline in vitro. This inhibition is caused by superoxide radicals that arise in the interaction of adrenaline with metal residues in an alkaline medium. The advantage of this method is that it can be used both for assessing the activity of SOD and for determining the antioxidant activity of biologically active materials, including extracts (Figure 3.2).

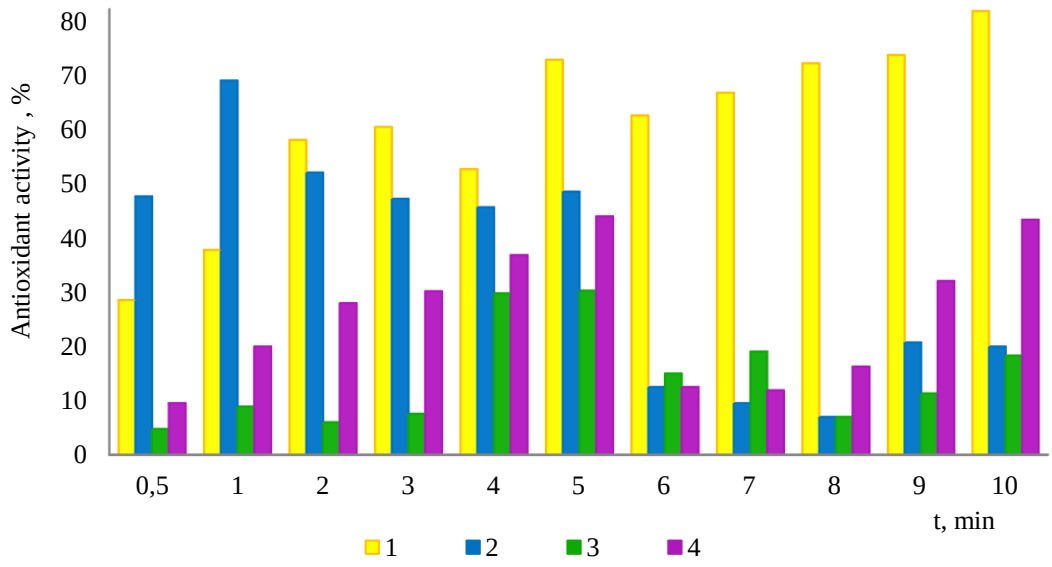

Figure 3.2. Antioxidant activity of plant extracts depending on the time of auto-oxidation of adrenaline in vitro: 1 – extract of calendula, 2 – extract of lavender, 3 – extract of wormwood, 4 – extract of lilac.

Data in Figure 3.2 show that all the extracts have a significant antioxidant effect, since the values obtained exceed the threshold value of 10%. The greatest antioxidant effect was reported for calendula extract. In the latter case, the activity increases significantly over time, and therefore this extract has a slow prolonged phase of oxidative-reducing potential.

Differences observed in the antioxidant properties of plant extracts by the two different methods can be explained by the sensitivity to different groups of biologically active substances. Thus, depending on the overall quantitative content of biologically active substances in plant extracts, they can have placed in a certain ranking order: lilac extract, calendula extract, lavender extract, extract of wormwood. The antioxidant activity determined by the FRAP method shows a direct relationship between the content of biologically active substances and the amount of antioxidant activity. In determining antioxidant activity on the ability to inhibit the auto-oxidation of adrenaline, the resulting dependence corresponds to the content of flavonoids in plant extracts.

Since the plant extracts studied have a high content of biologically active substances, they are potential active ingredients in cosmetic emulsions. The ability of extracts to influence the basic organoleptic, physical and chemical properties of cosmetic products, are given in Table 3.3.

Table 3.3. Organoleptic, physico-chemical parameters of cosmetic emulsion with extracts

Indicator	Cosmetic emulsion with extracts of				Base emulsion
	calendula	lavender	wormwood	lilac	
Appearance	Homogeneous texture with viscous consistency without extraneous impurities				
Color	White color, without foreign shades and inclusions				
Odor	Characteristic odor of cream				
Colloidal stability	Stable				
Thermal stability	Stable				
pH	7.1	7.5	7.2	7.4	7.1

Data in Table 3.3 indicate that the emulsion before and after the addition of investigated extracts meet the requirements specified in literature for cosmetics formulations[20,21].

The antioxidant properties of the emulsion with the addition of plant extracts was investigated and results are reported in Figure 3.3 and 3.4.

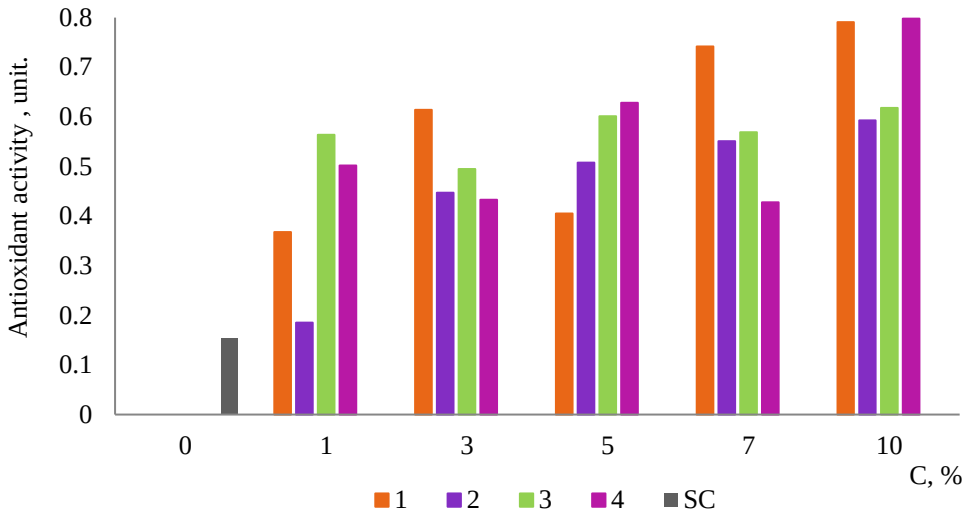

Figure 3.3. Dependence of antioxidant activity of samples of cosmetic emulsion on the concentration of plant extracts, determined by the method of FRAP: SC – solution for comparison, 1 – calendula extract, 2 – lavender extract, 3 – wormwood extract, 4 – lilac extract.

Figure 3.3 indicates that all plant extracts contribute to the growth of the antioxidant activity of the cosmetic emulsion relative to the base specimen, with the highest values observed at the largest concentration of extracts.

The dynamics of the antioxidant effect of the cosmetic emulsion at the maximum concentration of extracts (10%), determined by the ability of the emulsion with extracts to inhibit the auto-oxidation of adrenaline in vitro shown in Figure 3.4.

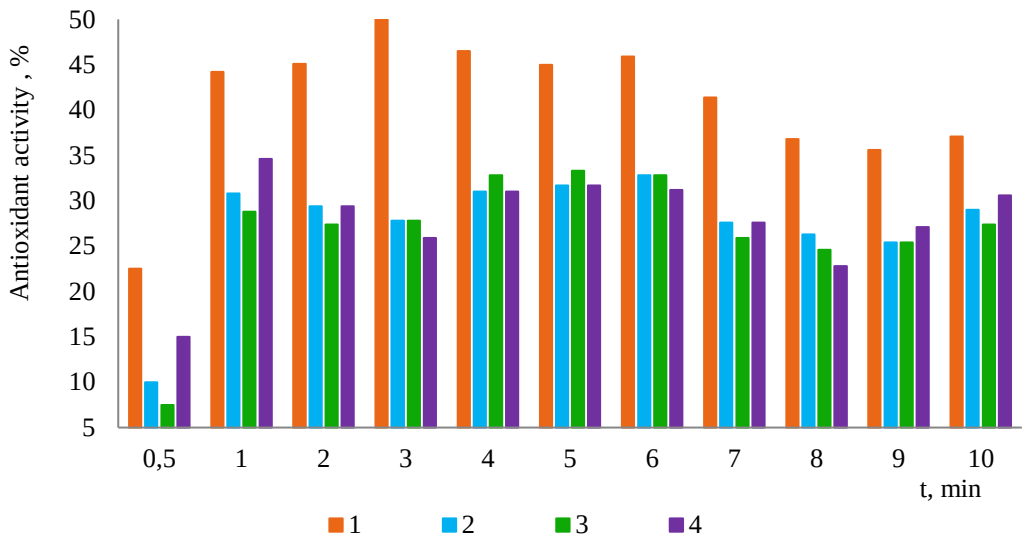

Figure 3.4. Antioxidant activity of a cosmetic emulsion with the content of plant extracts, depending on the time of auto-oxidation of adrenaline in vitro: 1 – calendula extract, 2 – lavender extract, 3 – wormwood extract, 4 – lilac extract.

Analysis of the data (Figure 3.4) shows that the highest and long antioxidant effect is the emulsion with an extract of calendula. Emulsions with extracts of lilac, lavender and wormwood have lower antioxidant activity, and almost identical with each other. It should be noted that the emulsion with an extract of calendula exhibits a more stable antioxidant effect.

The apparent dependence of the antioxidant activity of plant extracts on the content of biologically active is presented on the graph of correlation of Figure A.1. a, b. **(**Supplementary material**).**

Figure (A.1. a) indicates a direct relationship between the quantitative content of biologically active substances and the antioxidant activity index. In determining antioxidant activity on the ability to inhibit the auto-oxidation of adrenaline, the obtained dependence corresponds to the content of flavonoids in plant extracts (Fig. A.1. b). These results make it possible to make an assumption about the different sensitivity of methods to certain groups of biologically active substances.

The balanced natural complex of biologically active substances of individual extracts provides high

performance antioxidant activity, but the use of multiple extracts can cause reverse (prooxidant) effect. The antioxidant activity of cosmetic emulsions obtained by the FRAP method with combinations of several extracts and their comparative characterization with individual extracts are given in Table 3.4.

Table 3.4. The comparative characteristic of the antioxidant activity of samples of cosmetic emulsion with individual extracts and their combinations, determined by the FRAP method

Indicator	Optical density
Base emulsion	0.154
Individual extracts at concentration 10%	
Calendula	0.791
Lavender	0.593
Wormwood	0.618
Lilac	0.798
Combinations of extracts in the ratio of concentrations, %	
Calendula – Lilac (5: 5)	0.651
Calendula – Lavender (7: 3)	0.736
Calendula – wormwood (7: 3)	0.617
Lilac – Lavender (7: 3)	0.719
Lilac – wormwood (7: 3)	0.821

Results (Table 3.4) clearly show that all combinations of extracts increased antioxidant activity for emulsion with respect to the baseline sample. Note that a mixture of extracts of calendula and lilac showed antagonism effect towards each other. On the other hand, a mixture of extracts lilac – wormwood evidenced synergy in the antioxidant effect and it has the highest rates in comparison with the individual extracts.

4. Conclusions

4.1. The presence of water-soluble vitamins in the investigated plant extracts was established: B_1, B_3, B_5, P, C. The negative reactions on vitamins B_2 and B_6 have been substantiated.

4.2. It was proved that a larger share of polyphenols following plant extracts are flavonoids: flavones, flavanones, flavanols, flavanonols and halconies.

4.3. It has established that the antioxidant activity determined by FRAP shows a direct relationship with

the content of biologically active substances. In determining antioxidant activity on the ability to inhibit the auto-oxidation of adrenaline, the resulting dependence corresponds to the content of flavonoids in plant extracts. Such results can be explained by different sensitivity of the methods to certain groups of substances.

4.4. It has been determined that cosmetic emulsion with the addition of plant extracts have satisfactory organoleptic and physico-chemical characteristics.

4.5. It has been determined that the extracts of calendula, lavender and lilac have a strong antioxidant effect when used separately. Combinations of these extracts show worsening of performances. The extract of wormwood extract combined with lilac, conversely, manifests itself as active synergists towards biologically active substances contained in the extract of lilac.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Authors contributed equally.

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