

Stability studies of cosmetic emulsions prepared from natural products such as wine, grape seed oil and mastic resin



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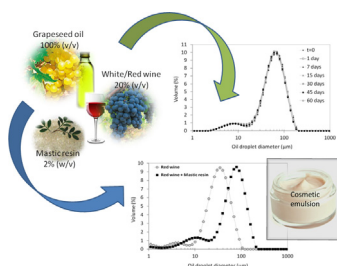
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HIGHLIGHTS

- Still wine and grapeseed oil can contribute natural components to cosmetic emulsions.
- Low wine concentrations yield rheologically stable O/W emulsions.
- The optimum wine percentage in the aqueous phase was found to be 20% (v/v).
- Mastic resin at 2% (w/v) is optimum for preparing O/W emulsions with grape seed oil.
- Combining wine and mastic resin results in bigger droplets and lower viscosity.

GRAPHICAL ABSTRACT



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ABSTRACT

An attempt was made in this study to use diluted wine as the aqueous phase and grapeseed oil as the oil phase for the preparation of oil-in-water cosmetic emulsions. Two monovarietal wines of Hellenic origin were used in this study; a red one from *Sangiovese* grapes and a white one from *Muscat of Samos* grapes. The oil-to-water ratio in the emulsions was 20:80 (v/v) and the wine concentrations in the aqueous phase were in the range of 5–100% (v/v). Glycerol monostearate was used as emulsifying agent. The only extra additive was mastic resin from *Pistacia lentiscus* var. *Chia*, which is reported to have healing and antibacterial properties. The study of the emulsion stability involved droplet size determinations and viscosity measurements for a period of sixty days. It was found that the optimum percentage of wine (red and white) in the aqueous phase of such emulsions is 20% (v/v) and of the mastic resin 2% (w/v).

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1. Introduction

During the last decade consumers have widely expressed their interest in natural products forcing the industry and the scientific

community to search for alternative sources and raw materials. Cosmetology is a highly affected area by this phenomenon and the use of natural components from olive oil to jojoba extracts forms the latest trend. One of the most significant reasons for this change is the appearance of allergies and skin irritations due to synthetic preservatives (e.g. parabens), colourants, stabilizers etc. that have not yet been fully tested in the long run for their consequences on consumers' health.

Wine and grapeseed oil are both natural products. Red wines especially have a high content in natural antioxidants such as

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flavanoids, natural colourants such as anthocyanins and natural aroma compounds such as terpenes and esters [1,2]. Grape seed oil on the other hand is considered to be a dietary oil of high quality with a high concentration of unsaturated linoleic acid, vitamin E and phytosterols [3,4]. In this study, an attempt was made to prepare oil-in-water cosmetic emulsions by adding white or red wine in the aqueous phase and using grape seed oil as the oil phase in order to examine their stability with time and exploit their beneficial constituents. The study was complemented by using the natural resin from the mastic tree of *Pistacia lentiscus* var. *Chia* as additive to examine its impact on the organoleptic and rheological characteristics of the emulsions. The mastic resin was chosen as a natural additive of Hellenic origin with healing and antibacterial properties [5–9].

2. Materials and methods

The oil-to-water ratio for the preparation of the emulsions was 20:80 (v/v) and commercial glycerol monostearate (GMS) was used as emulsifier at 6%, 8% and 10% (w/v). Two Hellenic wines, the white 'Samena Golden' from the grape variety 'Muscat of Samos' with 12.4% (v/v) ethanol and the red 'Sangiovese Karipidis 2002' from the grape variety 'Sangiovese' with 12.7% (v/v) ethanol were added at concentrations 5%, 10%, 20%, 50% and 100% (v/v) in deionised water to form the aqueous phase. Grapeseed oil (Henry Lamotte, Germany) was the oil phase in all cases. Mastic resin (Chios Mastiha Growers Association, Hellas) was added at concentrations 1%, 2% and 3% (w/v).

Emulsification was performed using an impeller with sawtooth edges placed for rotation in the centre of a 600-ml borosilicate-glass beaker and at approximately 1 cm above the bottom of the beaker. Initially, grapeseed oil was transferred to the beaker and heated at 70 °C. GMS was then slowly dissolved in the hot grapeseed oil. The aqueous phase was also heated separately in a conical flask at the same temperature and was subsequently added gradually to the oil phase under intense agitation at 400 rpm for 2 min. At this point, the heating was turned off and the emulsion formed was kept agitated until temperature dropped to 25 °C.

Applying this procedure, attempts were made to prepare emulsions with various combinations of the constituents described above. Out of these attempts, the following three series of 20:80 (v/v) O/W emulsions were successfully prepared:

- with grapeseed oil, 5–20% (v/v) white wine in the aqueous phase and 6% (w/v) GMS as emulsifier (series code: **W**); emulsions were not successfully prepared with 50% and 100% (v/v) white wine in the aqueous phase even when 10% (w/v) GMS was added.
- with grapeseed oil, 5–20% (v/v) red wine in the aqueous phase and 6% (w/v) GMS as emulsifier (series code: **R**); emulsions were successfully prepared also with 50% and 100% (v/v) red wine in the aqueous phase but only when 10% (w/v) GMS was added.
- with grapeseed oil, deionised water (i.e. 0% wine in the aqueous phase) and 1–3% (w/v) mastic resin as additive (series code: **M**).

In all cases, an O/W emulsion with 20:80 (v/v) grapeseed oil and deionised water was prepared as control sample (code: **C**).

The study of the emulsion stability involved the following procedures:

- Surface tension measurements of the aqueous phase using a Sigma 70 tensiometer (KSV Instruments Ltd., Finland) at 25 °C. The Wilhelmy plate technique was applied in the Wilhelmy Constant Run programme mode. A platinum plate was partially immersed into the surface layer of an aqueous phase and the

monitored surface tension decreased with time while the plate remained into position. The analysis ceased when the surface tension value was stabilized. Prior to each analysis, the surface tension of deionised water was measured as control.

- Interfacial tension measurements of the two-phase system using a K6 tensiometer (Krüss, Germany) at 25 °C. The Du Nouy ring method was employed. A platinum ring was used first to zero the indicator with grapeseed oil and then to measure the interfacial tension between grapeseed oil and each aqueous phase. Deionised water was used first as the aqueous phase for the reference measurement. Then followed the other aqueous phases which contained wine, measured from the most diluted one (5%, v/v wine) to the least diluted (100%, v/v wine). The interfacial tension of each system was measured at the point where the ring broke away from the interfacial layer of the two phases.
- Determination of the mean surface droplet diameter $D_{[3,2]}$ and droplet size distribution with the use of a Mastersizer 2000 with a HYDRO 2000MU unit (Malvern Instruments Ltd., UK). $D_{[3,2]}$ is the so called Sauter mean diameter and it is defined as the diameter of a sphere that has the same volume-to-surface area ratio as a particle or droplet of interest.
- Viscosity measurements with a LVTDV-II digital viscometer (Brookfield, USA) attached to a temperature controller (Poly-Science, USA) and using 25/13R accessories at 1.32 min⁻¹ and 25 °C. All measurements and macroscopic observations were performed at 0, 7, 15, 30, 45 and 60 days.

3. Results and discussion

As explained also in paragraph 2 (experimental part of Section 2), with the use of 6% (w/v) GMS as emulsifier, emulsions were successfully prepared with 5%, 10% and 20% (v/v) of red or white wine in the aqueous phase. In the case of higher wine concentrations, i.e. 50% and 100% (v/v), emulsification of grapeseed oil was achieved neither with the red nor with the white wine. However, by increasing the amount of the emulsifier up to 10% (w/v), emulsions were obtained only when using the red wine. For reasons of comparison among the various emulsions, the results discussed below refer only to the samples with 0–20% (v/v) wine (white or red) in the aqueous phase, and do not include the final two emulsions achieved with higher red wine and GMS concentrations.

3.1. Surface and interfacial tension measurements

Surface tension values of the aqueous phase of an emulsion are indicative data of the emulsion stability with time. Table 1 shows the corresponding values for each emulsion of the study. An alcoholic solution with 12% or 13% (v/v) ethanol has surface tension values $\gamma = 49.5$ mN/m and 48.1 mN/m, respectively [10,11]. In Table 1 it is shown that the surface tension values for 100% (v/v) wine with alcoholic grade around 12.5%, which is the average alcoholic grade of the two wines used in this study, are considerably lower than the above reference values. Even more surprising is the

Table 1
Surface tension values of the aqueous phases of the emulsions under study at 25 °C.

Aqueous phase Wine (% , v/v)	Surface tension γ (mN/m)	
	White wine	Red wine
100	42.0 ± 0.6	45.9 ± 0.8
50	48.6 ± 0.6	50.1 ± 0.8
20	51.0 ± 0.5	57.3 ± 0.7
10	54.0 ± 0.4	60.9 ± 0.4
5	62.9 ± 0.7	65.3 ± 0.9
0	71.6 ± 0.5	71.7 ± 0.4

Table 2

Interfacial tension values of the two-phase system of grapeseed oil and red/white wine in various percentages at 25 °C.

Two-phase system	Interfacial tension (mN/m)	
	White wine	Red wine
Oil phase:aqueous phase (20:80, v/v)		
GSO ^a (100%, v/v):wine (x%, v/v)		
x=100	6.4 ± 0.3	12.0 ± 0.4
x=50	10.4 ± 0.8	12.9 ± 0.4
x=20	15.3 ± 0.6	13.2 ± 0.8
x=10	17.5 ± 0.4	16.5 ± 0.6
x=5	20.2 ± 0.8	14.5 ± 0.6
x=0 (i.e. water 100%)	20.9 ± 0.2	20.9 ± 0.2

^a GSO: grape seed oil.

fact that the red wine exhibits higher surface tension than the white one (45.9 mN/m and 42.0 mN/m, respectively), although the former – being a red wine – has more phenolic compounds, proteins, etc. that could lower more its surface tension [11–17]. This finding can be attributed to the fact that the white wine used in this study is produced from a Muscat grape variety which is known for its high content in aromatic compounds. In any case, even with small percentages of wine – whether red or white – in the aqueous phase, e.g. 5% (v/v), the decrease of the surface tension value compared to that of water is significant.

The determination of the interfacial tension of a two-phase system can offer valuable information about the stability of an emulsion prepared from the particular two phases. In Table 2 the values of the interfacial tension between grapeseed oil and the different aqueous phases of the emulsions prepared with diluted wine, white and red, are presented.

It is shown that by adding white wine to reach 50% (v/v) in the aqueous phase, the interfacial tension between this phase and grapeseed oil decreases to half the value of the reference interfacial tension between grapeseed oil and water, i.e. from 20.9 mN/m to 10.4 mN/m. Even though the interfacial tension of the two-phase system is much lower for high concentrations of white wine than for the corresponding ones of red wine, it is noteworthy that emulsions were successfully prepared only with red wine at such high percentages. This means that although these two-phase systems of grapeseed oil and 50% or 100% (v/v) white wine appear to be physicochemically favoured, their interaction with the emulsifier GMS could result in unfavourable synergy for the preparation of stable emulsions. Further investigation of which wine components (polyphenols, polysaccharides, organic acids etc.) interact with GMS could elucidate the cause of this effect and will be planned for a future study.

3.2. Droplet size determination and viscosity measurements

It was macroscopically observed that none of the emulsions exhibited phase separation for over two months at room temperature. Nevertheless, the comparison of the droplet size distributions of each series obtained by laser light scattering revealed some insightful findings.

In the case of the first series of emulsions **W** (Fig. 1), the higher the white wine concentration in the aqueous phase was, the bigger were the oil droplet sizes, and more specifically the maximum point of their size distribution curve was shifted towards greater values.

These results are also in agreement with the data shown in Table 3 where the mean surface droplet diameters increase from lower to higher wine percentages and at the same time the viscosity of the respective emulsions decreases.

It was previously mentioned that all of the samples were found to be stable with time, as they did not exhibit creaming or phase separation. However and in particular, the emulsion with 20% (v/v) white wine in the aqueous phase produced almost identical droplet

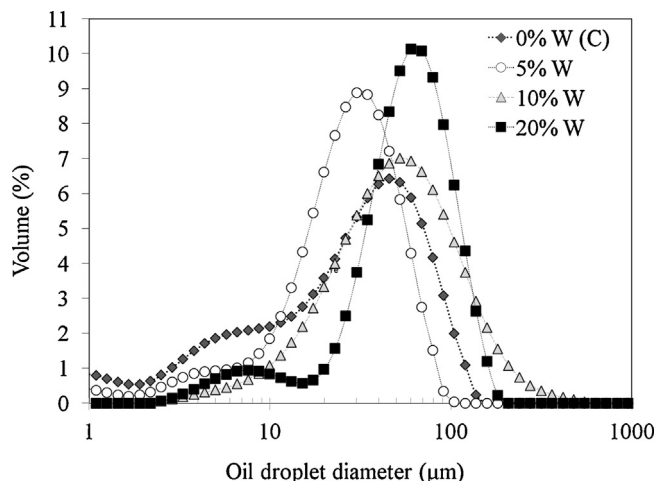


Fig. 1. Droplet size distribution curves of the emulsions with white wine in the aqueous phase (series **W**) at $t=24$ h.

size distribution curves throughout the whole study, as presented in Fig. 2. Therefore, compared with the other emulsions of the **W** series, the lack of droplet size fluctuations during storage renders this particular emulsion the most stable of them.

Similar results were found for the second series of emulsions with 5%, 10% and 20% (v/v) red wine in the aqueous phase (series **R**). In fact, the optimum – i.e. more stable – emulsion according to the droplet size distribution curves was also in this case the one with 20% (v/v) red wine. The type of its size distribution curves over a period of 60 days was very similar to the ones of Fig. 2 with the only difference being that their maxima appeared at smaller droplet sizes (approximately 35 μm for **R** and 60 μm for **W**). Moreover, the width of these size distribution curves (i.e. of the emulsion with 20% (v/v) red wine in the aqueous phase) was almost equal to that shown in Fig. 2 (i.e. of the curves of the emulsion with 20% (v/v) white wine in the aqueous phase). Another similarity of these two series of emulsions, **W** and **R**, was that the ones with red as well as the ones with white wine in the aqueous phase have produced larger oil droplets than the control emulsion **C** with 0% wine in the aqueous phase, as derived from Fig. 3 and Table 3.

The fact that for both series of emulsions, **W** and **R**, the optimum percentage of wine addition was 20% (v/v) could be attributed to the similar ethanol content of the two wines. It is generally accepted that ethanol often acts as co-surfactant reinforcing the films that surround the oil droplets [12,18]. Previous studies on

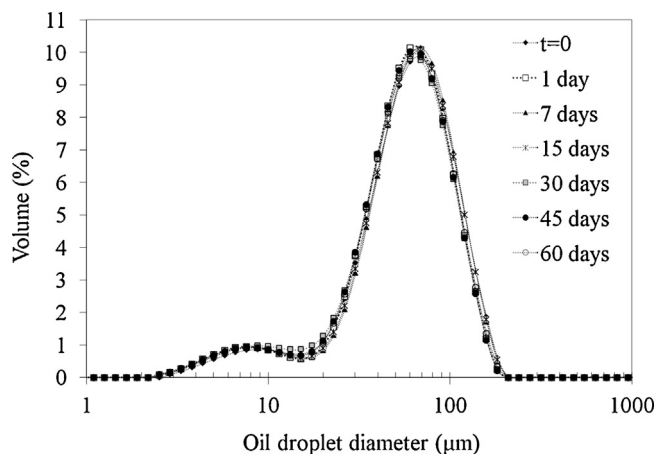
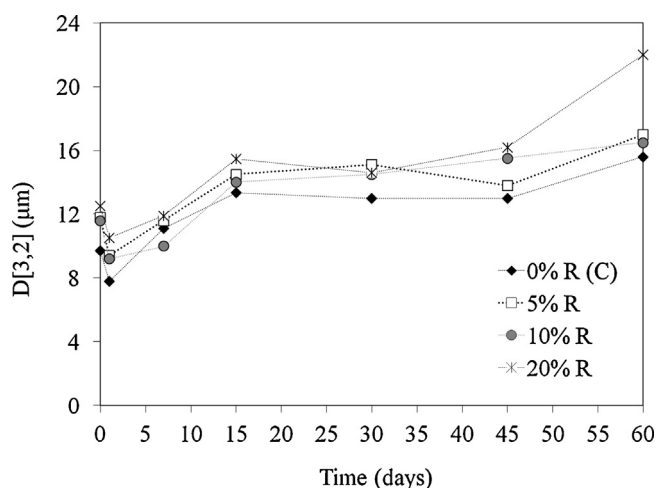


Fig. 2. Droplet size distribution curves of the emulsion with 20% (v/v) white wine in the aqueous phase for a period of $t=0$ –60 days.

Table 3Mean surface droplet diameter and viscosity values of the first series of emulsions with white wine in the aqueous phase (W) at 25 °C and $t=0-60$ days.

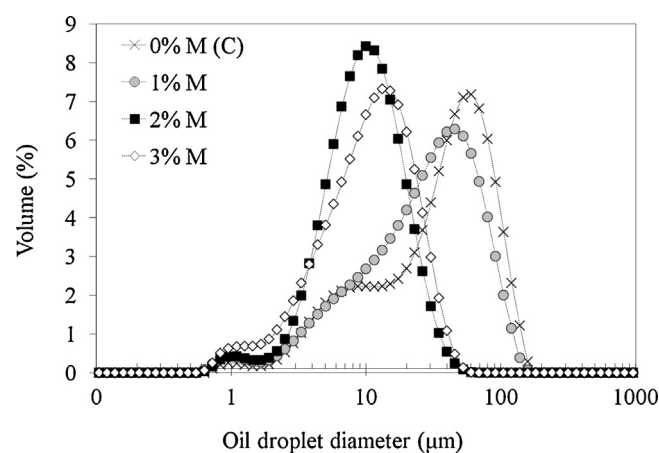
Time (days)	C 0%	W 5%	W 10%	W 20%	C 0%	W 5%	W 10%	W 20%
	Mean surface droplet diameter (μm)				Viscosity (mPa s)			
0	9.7 \pm 0.2	12.4 \pm 0.3	30.9 \pm 0.6	33.8 \pm 0.7	23.5	23.0	16.6	10.8
1	7.8 \pm 0.4	11.9 \pm 0.3	29.8 \pm 0.7	31.4 \pm 0.3	21.1	23.0	16.8	12.9
7	11.1 \pm 0.2	13.6 \pm 0.2	30.2 \pm 1.2	31.8 \pm 0.8	19.1	25.4	21.7	16.1
15	13.4 \pm 0.3	13.1 \pm 0.2	29.3 \pm 0.8	32.3 \pm 1.0	19.5	25.7	21.2	17.6
30	13.0 \pm 0.2	14.7 \pm 0.2	26.7 \pm 0.4	30.5 \pm 0.8	18.0	30.4	24.7	15.0
45	13.0 \pm 0.4	14.8 \pm 0.2	27.9 \pm 0.8	31.4 \pm 0.2	17.9	30.9	24.1	14.5
60	15.6 \pm 0.2	15.0 \pm 0.4	26.2 \pm 0.4	31.0 \pm 0.2	14.4	38.4	24.7	13.2

**Fig. 3.** Changes of the mean surface droplet diameter ($D_{[3,2]}$) of the second series of emulsions with red wine in the aqueous phase (series **R**) for $t=0-60$ days.

O/W emulsions that contained proteins in the aqueous phase have suggested that the addition of ethanol at 5–20% (v/v) interacts with the presence of electrolytes creating a stronger structure around the droplets [18]. The mechanism has been characterized as non specific and has been linked to the decrease of the dielectric constant of the matrix. In this way the water soluble constituents, like proteins and salts which are found in wine, are driven towards the droplet interfaces making the films more compact either through electrostatic forces or by diminishing the stereochemical obstructions [18]. This has been observed only for limited ethanol and electrolyte concentrations because at higher percentages phase separation is most likely to occur. The same studies have shown that the higher the ethanol content in such emulsions, the lower their viscosity values and the higher their droplet sizes [18,19], exactly as presented in Table 3 of the present study for increasing wine concentration.

Having the above information in mind, when the initial ethanol concentration of a wine is approximately 12.5% (v/v), the optimum 20% (v/v) of wine addition in O/W emulsions corresponds to 1/5 of the 12.5% of ethanol and that equals with 2.5% (v/v) of ethanol concentration in the emulsion. Therefore, the above results indicate that the optimum ethanol percentage in such emulsions is 2.5% (v/v). The effect of this ethanol concentration on the droplet size and the viscosity of the emulsions of this study is justified by bibliographic data and could account for the unsuccessful preparation of emulsions with 50% and 100% (v/v) of white wine in the aqueous phase (especially in view of its overall chemical composition including protein and potassium content, which were found to be lower than those of the red wine – data not shown).

The effect of wine composition and particularly of the ethanol content on the successful preparation of emulsions, as explained above, applies also to the case of the red wine series (**R**) with the

**Fig. 4.** Droplet size distribution curves of the 20:80 (v/v) O/W emulsions with 1–3% (w/v) mastic resin (series **M**), at $t=15$ days.

exception that by using more emulsifier (10% (w/v) GMS) it was made possible to prepare emulsions with 50% and 100% (v/v) wine in the aqueous phase. This would be generally desirable because more antioxidants and natural pigments would be contained in the final product. However, the use of more emulsifier in order to achieve emulsification resulted in a very dense texture of the emulsion with 50% (v/v) red wine, impeding the product's application on the skin. On the other hand, the emulsion with 100% (v/v) red wine in the aqueous phase had a very watery texture and remained stable without exhibiting phase separation for only fifteen days. Nevertheless, the macroscopic observation of both of these emulsions concluded that the increased percentage of red wine hindered any fungus appearance and mould formation. This observation could be attributed to the sufficient amount of phenolic compounds such as tannins and *p*-hydroxy-benzoic acid derivatives that are contained in red wine and could act as natural antioxidants and preservatives [20–22].

Drawn from the texture differences observed in the above emulsions, a third series of emulsions was prepared only with mastic resin as additive and initially without wine in the aqueous phase (series **M**). The resin from the mastic tree *Pistacia lentiscus* var. *Chia* was selected for this purpose in an attempt to optimize the organoleptic characteristics of the emulsions, i.e. mainly their texture and odour. It is reported that both the resin and the essential oil derived from the *Pistacia lentiscus* var. *Chia* plants, which grow only on the island of Chios in Greece, have antibacterial and healing properties; consequently, this type of mastic resin that was chosen for the present study is listed as a Hellenic natural product of high value [6–9].

In Fig. 4, the droplet size distribution curves of the **M** series of emulsions are presented. The time period of fifteen days was chosen for these plots as it was the most indicative of the changes that occurred in the oil droplet sizes. It is evident that the

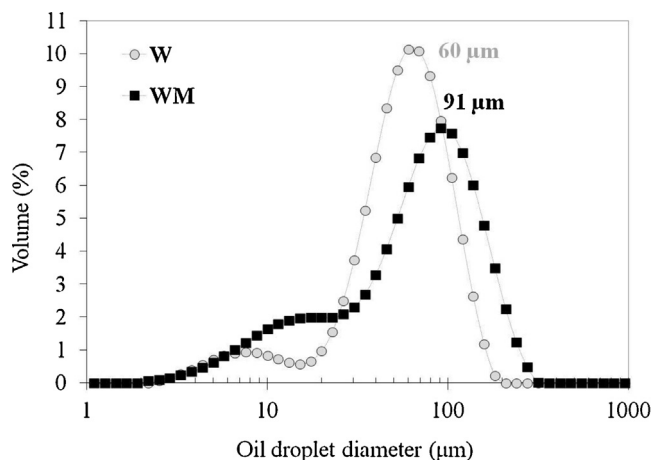


Fig. 5. Comparison of the droplet size distribution curves between the emulsions with 20% (v/v) white wine in the aqueous phase and with (WM) or without (W) 2% (w/v) mastic resin, at $t = 24$ h.

narrowest distribution corresponds to the emulsion with 2% (w/v) mastic resin and the maximum of its curve corresponds to the smallest droplet diameter ($10\ \mu\text{m}$) of the graph. This result suggests that the particular emulsion would be stable with time in terms of droplet coalescence and ultimately phase separation. When the initial size of the droplets is rather small and remains small with time, their coalescence rate could be considered low under certain conditions, otherwise the mean droplet diameter would increase. This finding indicates that the films that surround the droplets in the particular emulsion are quite durable and resistant [23]. In fact, the same emulsion exhibited the fewest changes in droplet size distribution over the sixty-day period of the study (data not shown) and, consequently, it was considered to be the most stable of the third series (M). For this reason it was chosen for further tests in combination with white and red wine. More specifically, the optimum emulsion in terms of stability was selected from each series (W, R and M) and two new test emulsions were prepared as a combination of their constituents; one emulsion with 20% (v/v) white wine in the aqueous phase and 2% (w/v) mastic resin as additive, and a second emulsion with 20% (v/v) red wine in the aqueous phase and 2% (w/v) mastic resin.

In the first case of the emulsions with the white wine (Fig. 5), the droplet size distribution curves have shown that mastic resin causes a shift to bigger droplet diameters (approx. $91\ \mu\text{m}$ for WM as opposed to approx. $60\ \mu\text{m}$ for W, at the corresponding maxima) and broadens the size distribution. In the second case of the emulsions with the red wine (Fig. 6), the mastic resin appears to have a less profound effect on the form of the droplet size distribution curve (the two curves have similar shapes) but the maximum is also shifted to a higher diameter value compared to that of the emulsion without the mastic resin (approx. $79\ \mu\text{m}$ for RM as opposed to approx. $35\ \mu\text{m}$ for R). The fact that the oil droplets are enlarged in both emulsions due to the presence of the resin could be explained by its composition which includes macromolecules of poly(β -myrcene) and voluminous molecules of condensed aromatic rings [5]. These molecules could interact with glycerol monostearate (GMS) participating in the film structure and because of their bulky stereochemistry they expand it. However, the observed increase of the oil droplet size in the presence of the resin did not lead to destabilization of the two-phase systems, as indicated by droplet size data (not shown) based on which the droplets sustained their sizes throughout the sixty-day period, i.e. they did not flocculate or coalesce.

Furthermore, as shown in Fig. 7, the emulsions with white wine (W and WM) have lower viscosity values than the ones with red

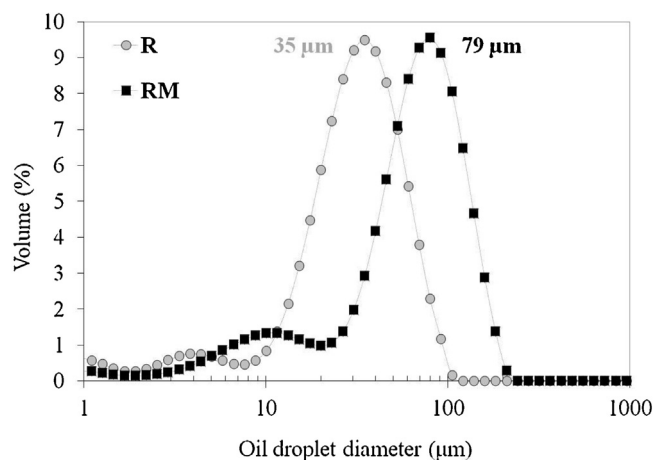


Fig. 6. Comparison of the droplet size distribution curves between the emulsions with 20% (v/v) red wine in the aqueous phase and with (RM) or without (R) 2% w/v mastic resin, at $t = 24$ h.

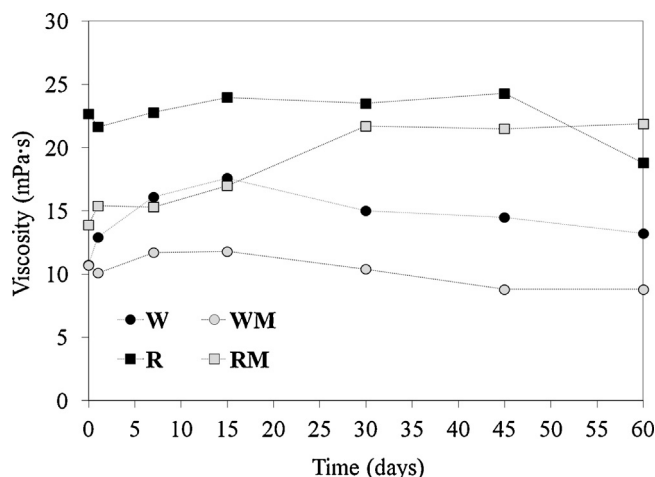


Fig. 7. Viscosity values of the emulsions with 20% (v/v) white or red wine and with (WM and RM, respectively) or without (W and R, respectively) 2% (w/v) mastic resin, at $25\ ^\circ\text{C}$ and $t = 0$ –60 days.

wine either in the absence or presence of the mastic resin (R and RM, respectively). These data are in agreement with the corresponding mean surface droplet diameters which were generally smaller for the emulsions with the red wine, effecting higher viscosity to them [23,24]. It is also noteworthy that when the mastic resin was present, the viscosity of the emulsions (WM and RM) was lower than that of the corresponding emulsions without the resin (W and R, respectively). Combining the above results it is concluded that the mastic resin increased the oil droplet sizes and lowered the viscosity values but did not destabilize the emulsions with time as to cause phase separation. Macroscopic observations supported this conclusion indicating that the structure of the emulsions was not made less cohesive, just softer. In addition, no extensive superficial mould was observed neither on the emulsions prepared only with deionised water and 1–3% (w/v) mastic resin nor on the ones with white/red wine and mastic resin.

4. Conclusions

Preparation of O/W cosmetic emulsions with grapeseed oil and diluted white or red wine in the aqueous phase presents certain advantages, such as direct inclusion of natural antioxidants, aroma and colour compounds in the emulsions that could enhance their

organoleptic characteristics. In this study, it was found that the optimum percentage of wine addition in the aqueous phase is 20% (v/v) for both a red Sangiovese and a white Muscat wine with mean alcoholic grade 12.5% (v/v). At low wine concentrations, all emulsions were rheologically stable for a period of at least two months. The absence of mould formation and other surface alterations when higher concentrations of red wine were used could be attributed to the wine's high content in phenolic compounds which have antioxidant capacity, including a sufficient concentration of *p*-OH-benzoic acid derivatives which could act as natural preservatives.

The use of mastic resin from *Pistacia lentiscus* var. *Chia* as additive in O/W cosmetic emulsions with grapeseed oil resulted in refined texture and odour of the emulsions prepared. The optimum percentage of addition was found to be 2% (w/v). In combination with diluted white or red wine in the aqueous phase, the mastic resin yielded emulsions with higher oil droplet diameters and lower viscosity values but it did not lead to phase separation of the two-phase systems. Further studies could investigate whether at the concentration added, the mastic resin imparts also antibacterial properties to the emulsions studied.

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