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MICROENCAPSULATION OF BERGAMOT PEEL ESSENTIAL OIL WITH GUM ARABIC AND MALTODEXTRIN BLENDS: STABILITY AND RELEASE CHARACTERISTICS OF THE ESSENTIAL OIL COMPOUNDS

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ABSTRACT

Bergamot peel essential oil is a high value product which can be used in food, beverage, confectionary, and cosmetic industries. Bergamot essential oil has high volatility, so it could be easily affected by environmental factors so it should be protected with further techniques to increase its shelf-life. The aim of this study was to examine the effect of different wall material compositions on the product yield, encapsulation efficiency, physical and chemical properties of encapsulated oil powders. For this purpose, bergamot essential oil was encapsulated with gum arabic and maltodextrin (DE 12) in varying concentrations (100:0, 0:100, 25:75, 75:25, 40:60, 60:40). Then, physical and chemical (terpenoid composition) characteristics of microcapsules were evaluated. The microcapsules were stored at 25°C for 20 days and the content and stability of main aroma compounds were determined after storage. The encapsulation yield was increased when the maltodextrin ratio was increased however, gum arabic provided greater protection of essential oil composition.

Keywords: Bergamot (*Citrus bergamia*), essential oil, aroma, microencapsulation, gum arabic, maltodextrin, spray drying

BERGAMUT UÇUCU YAĞININ ARAP ZAMKI VE MALTODEKSTRİN KARIŞIMLARI KULLANILARAK MİKROENKAPSÜLASYONU: UÇUCU YAĞ BİLEŞENLERİNİN STABİLİTE VE SALINIM ÖZELLİKLERİNİN BELİRLENMESİ

ÖZ

Bergamut uçucu yağı, gıda, içecek, şekerleme ve kozmetik endüstrilerinde kullanımı olan değeri yüksek olan bir uçucu yağdır. Yüksek uçuculuğu ve çevresel etkilere karşı duyarlılığı nedeniyle, bergamut uçucu yağının raf ömrü boyunca stabilitesini korumak için koruyucu önlemler alınması gerekmektedir. Bu çalışmanın amacı, farklı taşıyıcı materyallerle kapsüllenmesi, ve bu materyallerin mikrokapsüllerde ürün verimi, kapsülleme verimi, fiziksel ve kimyasal özellikler üzerine etkilerinin incelenmesidir. Bu amaçla, farklı konsantrasyonlarda (100: 0, 0: 100, 25:75, 75:25, 40:60, 60:40) arap zamkı ve maltodekstrin (DE 12) kullanılarak bergamut uçucu yağı kapsüllenmiştir. Elde edilen bergamut uçucu yağı mikrokapsüllerinin fiziksel ve kimyasal (terpenoid kompozisyonu) özellikleri değerlendirilmiştir. Ayrıca, mikrokapsüller 25°C'de 20 gün boyunca depolanmış ve depolamadan sonra önemli uçucu yağ bileşenlerinin içeriği ve stabilitesi belirlenmiştir. Emülsiyonlarda, maltodekstrin oranı arttığında ürün verimi artmıştır ancak arap zamkı, uçucu yağ bileşiminin daha iyi korunmasını sağlamıştır.

Anahtar kelimeler Bergamut *(Citrus bergamia)*, kabuk uçucu yağı, aroma, kapsülleme, arap zamkı, maltodekstrin , püskürterek kurutma

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INTRODUCTION

Bergamot (*Citrus Bergamia*) is a citrus plant and it is extensively cultivated as evergreen ornamental three in Mediterranean Region of Turkey. Peels of ripe bergamot fruit are mainly used in jam and essential oil production. The essential oil is a high value product and it is widely used in food, beverage, confectionary, perfumery and cosmetic for its fragrance and freshness (Navarra et al., 2015). Nowadays it is an valuable essential oil due to its hypolipidemic and hypoglycaemic activity (Mollace et al., 2011), as well as antiinflammatory (Impellizzeri et al., 2015) and anti-cancer properties (Navarra et al., 2015; Visalli et al., 2014).

Bergamot essential oil has high volatility, so it could be easily affected by environmental factors so it should be protected with further techniques to increase its bioavailability, functional properties and shelf-life. Microencapsulation is the most commonly used technique to protect various types of food ingredients, such as essential oils, flavors, vitamins, pigments etc. from detrimental conditions (i.e. light, heat, moisture). Numerous encapsulation techniques have been developed, but spray drying is the most widespread one for the production of dry flavorings (Jafari et al., 2008; Roos and Karel, 1991). An emulsion composed of water, carrier, and flavor is prepared and then atomized into a stream of hot air. The atomized particles are rapidly dried in a drying chamber. The volatile constituents are trapped inside the droplets during the process (Reineccius, 2004). Encapsulation efficiency could be affected from drying conditions, wall materials and core material properties such as viscosity and concentration (Jafari et al., 2008).

Composition of wall materials and drying operational conditions directly influence the final product. There are lots of wall materials such as; mono and disaccharides, hydrolysed starches (maltodextrins and corn syrup solids), chemically modified (emulsifying) starches, gums and proteins (Jafari et al., 2008; Turchiuli et al., 2005). Among these wall materials, gum arabic (acacia gum) is the most widely used for encapsulating flavors and oils. It could protect volatiles during spray drying processes (Fuchs et al., 2006). However, it has some problems; such as; high cost and stickiness during spray drying etc. On the contrary, maltodextrin offers many advantages such as low viscosity, low cost, bland flavor, high water solubility (Carneiro et al., 2013; Jafari et al., 2008). But it has low emulsification capacity. So, using maltodextrin in combination with gum arabic could provide an effective microencapsulation by spray drying.

There are several studies on bergamot peel essential oil composition and its antimicrobial properties (Costa et al., 2010; Ghabraie et al., 2016; Ribes et al., 2017; Yang et al., 2018). In an only study, carried out by Penbunditkul et al. (2012), shows that high pressure homogenization process with modified starch were not suitable to prepare bergamot oil emulsion. However, to our knowledge, there is no any other study on bergamot essential oil microencapsulation to achieve high microencapsulation efficiency and stable product. Therefore, the scope of this study included: (a) determining the aroma composition of bergamot essential oil obtained from the fruits grown in the region Antalya-Turkey, (b) investigating the most appropriate gum arabic and maltodextrin composition on the behalf of encapsulation and product efficiency, (c) determining the effect of encapsulation process on the chemical composition of bergamot essential oil, (d) testing physical properties of bergamot essential oil microcapsules and (e) evaluating the aroma stability of obtained microcapsules after 20 days of storage at 25ºC.

MATERIALS AND METHODS

Wall and core materials

Gum arabic (AG) and Maltodextrin Glucidex with a dextrose equivalent of 12 (MD) were purchased from Sigma–Aldrich (Germany) and Roquette (France), respectively. Bergamot fruits were randomly picked up in fully mature state from the orchard of West Mediterranean Research Institute (Antalya, Turkey), and their flavedo parts were grated by hand grater. The grated bergamot rinds were used for essential oil production.

Methods

Extraction of bergamot essential oil

The oil was obtained by steam distillation of the grated bergamot rinds. The obtained oils were stored in air-tightly sealed amber vials at -18 °C until analyses and spray drying microencapsulation process.

Preperation of Emulsions

Emulsions were prepared according to procedure of (Turchiuli et al., 2005). Emulsions of the bergamot essential oil were prepared in six different AG/MD blends given in Table 1. The blends of gum arabic (AG) and maltodextrin (MD) were dissolved in distilled water at a concentration of 30g/100mL. The essential oil (5% w/w of the dry matter) and Tween 80 (1% v/w dry matter) were added into the hydrated wall material solutions. Tween 80 added as an emulsifier to increase emulsion stability. The dispersions were magnetically stirred for 5 min to form a coarse pre-emulsion then they were homogenized using an UltraTurrax homogenizer (TA 25, IKA, Janke & Kunkel GmbH&Co, Germany) at 13000 rpm for 4 min.

Table 1 Composition of the emulsions used in the microencapsulation processes

Emulsions	AG:MD ratios	Wall materials (%)	Core: Wall material ratios (w/w)
B1	100:0	30	5:100
B2	0:100	30	5:100
B3	25:75	30	5:100
B4	75:25	30	5:100
B5	40:60	30	5:100
B6	60:40	30	5:100

Microencapsulation Process by Spray Drying

The emulsions were spray-dried using a co-current Mini Spray Dryer B-290 (BUCHI Labortechnik AG, Flawil, Switzerland) equipped with a two-fluid nozzle atomizer. Operation conditions were: atomization air flow rate of 500 L/h (5 bar), inlet air temperature of 200°C and outlet air temperature of 110°C. Emulsions were fed to spray dryer at room temperature and at adjusted flow rate between 450-750 mL/ hour to keep constant outlet temperature. The microcapsules obtained from each experiment were collected from collection vessel.

Characterization of the microcapsules

Moisture content and water activity

Moisture content of the microcapsules was determined by the toluene distillation method (Bertolini et al., 2001). Eight grams of powder were added to 200 mL toluene in 250 ml flask and distilled for 3 hours. The volume of collected water was read directly from graduated side and results were calculated as percentage of microcapsules' weight.

Water activity of the microcapsules was determined by using water activity meter (TESTO650). Two grams of powder was placed into sample holder of the device. After moisture equilibration at room temperature (25°C±1) water activity value was recorded.

Bulk density

Bulk density was determined by the tapping method (Beristain et al.,2001). Two grams of the microcapsules weighed into 20 mL graduate cylinder and the cylinder was tapped automatically for 20 times. The final volume of the microcapsules was recorded and bulk density was calculated by dividing the sample weight by the volume.

Particle size distribution of the microcapsules

Particle size distribution of the microcapsules was determined by light scattering technique using a particle size analyser (Mastersizer 2000, Malvern, Worcestershire, UK) equipped with a dry powder dispersion unit (Scirocco 2000). Particle size distributions of the microcapsules were

determined as volume-based D(0.5) and D(0.9) values which represent 50 % and 90 % of the total particle population, respectively (Zhang et al., 2012).

Encapsulation efficiency and yield

In order to determine the encapsulation efficiency, the essential oil was recovered from the microcapsules by steam distillation method (Bousbia et al., 2009). Ten grams of the powder was dissolved in 150 mL distilled water. Then the solution was distilled for 3 hours to carry over the recovered essential oil to the graduated arm. The recovered essential oil volume was recorded and converted to weight by its density. The encapsulation efficiency (EE) and encapsulation (product) yield (EY) were determined as follows:

$$EE = \frac{M\ oil\ encapsulated}{M\ oil\ to\ be\ encapsulated} \times 100\%$$

$$EY = \frac{M\ microcapsules}{M\ total} \times 100\%$$

where $M\ oil\ encapsulated$ is the actual amount of encapsulated bergamot essential oil (g), $M\ oil\ to\ be\ encapsulated$ is the theoretical mass of bergamot essential oil to be encapsulated in the emulsions, $M\ microcapsules$ is the mass of final product (g), $M\ total$ is the total mass of initial wall and core materials (g).

Effect of microencapsulation on the chemical composition of bergamot essential oil

The composition of the bergamot essential oil was determined before and after the spray drying process according to the method used by Verzera et al. (2003). The analyses were performed on a gas chromatography-mass spectrometry (GC-MS) (Shimadzu QP 2010) equipped with fused silica capillary column (30 m × 0.25 mm i.d., coated with TRB 5 MS, 0.25 μm film thickness). The column temperature was programmed to rise from 40 to 240 °C at constant rate of 3 °C/min. The carrier gas was He with a linear flow rate of 42.7 cm/s (90 kPa). The essential oil oil was diluted in hexane (1:25, v/v) and 1 μL of this solution was injected into the injection port maintained at 250 °C. The injection mode was split with the ratio of 1:25; MS scanning was accomplished at 250 °C, ionizing voltage was 70 eV and mass scan range was 40–400 D, m/z. Chromatograms were automatically integrated by ignoring small peaks that less than 100.000 mV. Identification was performed by GC–MS analysis, mass spectra for each peak were compared with those in the published index data library FFNSC GC/MS Library ver. 1.2. of the GC–MS equipment. All compounds were confirmed with retention indices of published mass spectra (Verzera et al., 2003).

Stability of major essential oil components in the microcapsules

Ten grams of microcapsules was weighed into a petri dish and placed in desiccators which has maintained to 33 % RH at 25ºC by magnesium chloride. The desiccators were sealed and held in an incubator at 25ºC for 20 days. After 20 days of storage, the essential oil in the microcapsules was recovered and its composition was analysed by GC-MS. The main monoterpenes (α-pinene, myrecene, limonene, γ-terpinene, linalool, α – terpineol, geranyl acetate) of the recovered essential oils were detected and quantified.

Statistical Analysis

The experiment was designed as a randomized plot. The microencapsulation processes were carried out in two replicates and analyses were performed in duplicates. Results were presented as mean values with standard deviations (mean ± SD). Statistical significance (P <0.05) was determined with one-way analysis of variance and differences between mean values were evaluated by using Duncan's multiple range test (ANOVA) using the SAS software (SAS institute, Cary, NC, USA).

RESULTS AND DISCUSSION

Chemical composition of the bergamot essential oil before and after microencapsulation

Thirty compounds were identified and quantified in the bergamot essential oil soon after distillation (Table 2). The main compounds detected in bergamot essential oil were; limonene (40.92%), linalyl acetate (19.20 %), linalool (17.41 %), γ - terpinene (6.21 %), β-pinene (4.47%), alpha-terpineol (2.13%), myrecene (1.70%), geranyl

acetate (1.08%), α- pinene (1.04%) and neryl acetate (0.94%). Similar to our results, Sawamura et al. (2006) detected; linalyl acetate (30.1%), limonene (37.2%), γ-terpinene (6.8%), linalool (8.8%), and β-pinene (6.12%) as main components in cold-pressed bergamot oil. The ratio of linalool to linalyl acetate is known as "essence degree" and it is one of the quality parameter of bergamot essential oil. The essence degree was 0.90 in the present study but has been reported to be approximately 0.3 in bergamot oil produced in Reggio Calabria which is known for its high quality (Sawamura et al., 1999). This could be related with the region, harvest time and distillation technique. Eleni et al. (2009) reported that the degree was 0.38-0.59 in cold pressed oil while it was 2.96 in hydrodistillated oil. Similarly, Bousbia et al. (2009) found the value of this ratio is 0.6 in hydrodistillated Tunisian *Citrus bergamia* peel oil and reported that the oil presented better essence degree than Calabria essential oil.

Table 2 Composition of the bergamot essential oil

Peak #	RI	Compound	Retention time (min)	Q*(%)	Area(%)
1	926	α- Thujene	9.305	98	0.26
2	933	α –Pinene	9.540	98	1.04
3	971	Sabinene	11.305	99	0.76
4	973	β-Pinene	11.383	98	4.47
5	992	Myrcene	12.214	98	1.70
6	1003	α- Phenalldrelene	12.725	85	0.05
7	1012	Hexyl acetate	13.037	90	0.04
8	1018	α -terpinene	13.289	96	0.28
9	1023	p- Cymene	13.659	98	0.59
10	1030	Limonene	13.992	96	40.92
11	1039	(Z) - β -Ocimene	14.428	92	0.15
12	1049	(E)- β –Ocimene	14.901	98	0.43
13	1058	γ -Terpinene	15.327	97	6.21
14	1087	Terpinolene	16.689	97	0.38
15	1103	Linalool	17.453	98	17.41
16	1105	Nonanol	17.575	90	0.06
17	1175	Terpinen-4-ol	20.868	93	0.18
18	1189	α - Terpineol	21.529	97	2.13
19	1206	Decanal	22.331	94	0.03
20	1214	Caprylyl acetate	22.703	98	0.09
21	1228	Nerol	23.359	98	0.36
22	1240	Neral	23.888	96	0.27
23	1259	Linalyl acetate	24.780	97	19.20
24	1270	Geranial	25.266	97	0.39
25	1349	Terpinyl acetate	28.743	97	0.14
26	1366	Neryl acetate	29.479	98	0.94
27	1385	Geranyl acetate	30.305	98	1.08
28	1417	β-Caryophyllene	31.657	89	0.14
29	1436	trans-α-Bergamotene	32.433	97	0.14
30	1509	Bisabolene <beta->	35.420	97	0.19

Table 3 shows the composition of essential oils recovered from the microcapsules. The main compounds were limonene (39.39-43.58%), linalool (18.37-22.68%), γ-terpinene (6.20-6.61 %), sabinene+β-pinene (3.75-4.68 %), α–terpineol (3.30-5.26%), geranyl acetate (2.29-3.09%) myrecene (1.86-2.29 %) and neryl acetate (1.60-2.03%). These results clearly showed that

some essential oil components markedly changed depending on the wall material composition. This notable difference was particularly determined in linalyl acetate content. This component was 19.20 % in the bergamot essential oil, however; it ranged between 5.42% and 13.33% in the powders as jointly determined with geraniol. Geraniol, which could not be detected at the beginning in bergamot essential oil, was determined significant amount in the essential oil recovered from the microcapsules. This difference could be explained with partial decomposition of linalyl acetate to geraniol due to the thermal degradation during spray drying. Linalyl acetate degraded with thermal effect and lead to linalyl, geranyl and neryl carbocation which activates considerable rearrangement reactions and form linalool, geraniol and nerol. Moreover, linalyl acetate can be changed into geranyl acetate and neryl acetate and converted into acyclic monoterpene hydrocarbons such as myrcene, cis- and trans-β-Ocimenes by elimination (Casabianca et al.,1998; Mastelic and Jerkovic, 2003). According to our results, the highest geraniol+ linalyl acetate content were determined in B5 (13.33 %, AG:MD;40:60) sample, followed by B1 (11.89 %, AG:MD;100:0) and B4 (10.38 %, AG:MD;75:25) samples. The amount of myrecene, neryl acetate and geranyl acetate contents also increased in all the microcapsules in comparison to the bergamot essential oil.

Table 3 Composition of the bergamot essential oils recovered from the microcapsules

NO	Compound name	Microcapsules					
		B1	B2	B3	B4	B5	B6
1	α- Thujene	0.22	0.14	0.16	0.19	0.20	0.18
2	α- Pinene	0.90	0.75	0.74	0.83	0.80	0.81
3	Sabinene + β-pinene	4.68	3.75	3.87	4.50	4.37	4.14
4	Myrcene	1.86	2.21	2.21	2.03	1.92	2.29
5	α-Phellandrene	0.06	0.07	0.06	0.06	0.06	0.06
6	α- Terpinene	0.29	0.38	0.35	0.31	0.31	0.36
7	p-Cymene	0.60	0.76	0.75	0.81	0.74	0.99
8	Limonene	43.22	41.62	40.19	39.70	39.39	41.87
9	(Z) – β-Ocimene	0.34	0.45	0.45	0.39	0.36	0.48
10	(E)- β-Ocimene	0.79	1.01	1.02	0.90	0.86	1.08
11	γ-Terpinene	6.59	6.49	6.22	6.20	6.62	6.43
12	Terpinolene	0.53	0.75	0.69	0.59	0.59	0.69
13	Linalool	18.37	20.99	22.25	21.01	19.01	22.76
14	Nonanal	-	-	0.04	-	-	-
15	Terpinen-4-ol	0.21	0.48	0.42	0.31	0.26	0.38
16	α -Terpineol	3.30	5.41	5.26	4.34	3.54	4.67
17	Decanal	0.04	0.06	0.06	0.05	0.06	0.05
18	Capryl acetate	0.11	0.13	0.14	0.13	0.15	0.13
19	Nerol	0.58	0.92	1.01	0.81	0.70	0.80
20	Neral	0.28	0.31	0.35	0.32	0.35	0.28
21	Geraniol +Linalyl acetate	11.89	7.46	6.95	10.38	13.33	5.42
22	Geranial	0.42	0.46	0.50	0.45	0.50	0.38
23	Terpinyl acetate	0.19	0.17	0.19	0.21	0.24	0.17
24	Neryl acetate	1.60	1.83	2.03	1.99	2.03	1.89
25	Geranyl acetate	2.29	2.75	3.09	2.89	2.76	2.90
26	β-Caryophyllene	0.20	0.19	0.20	0.23	0.27	0.21
27	Bergamotene α- trans	0.21	0.19	0.20	0.22	0.27	0.23
28	β-Bisabolene	0.27	0.26	0.27	0.30	0.37	0.30

*Q: Similarity ratio.

Linalyl acetate also produces monocyclic monoterpenes hydrocarbon– terpinolene – as the main product from linalyl acetate via the α-terpinyl cation and terpinen-4-yl cation. α-terpineol and then 1,8-cineole can be formed by hydration of the a-terpinyl cation. Besides, terpinene-4ol can be formed by the hydration of the terpinene-4-yl cation. After encapsulation, terpinolene, tepinene-4-ol and α-terpineol increased in all microcapsules. These changes can be proportional increases, which can be related with removal of the other components during the process. The oil compositions detected in B4 (AG:MD; 75:25) and B5 (AG:MD; 40:60) microcapsules were the least affected from encapsulation process. The ratio of α-terpineol in microcapsules obtained with both only maltodextrin and gum arabic/maltodextrin (25:75) blend was determined two times higher than that of bergamot essential oil. Similar to our results, Penbunditkul et al. (2012) reported that different wall materials and saturation of wall materials affected the flavour retentions and surface oil content of encapsulated multi-flavour bergamot oil.

Encapsulation yield and efficiency

The effect of gum arabic and maltodextrin concentrations on encapsulation yield (EY) and encapsulation efficiency (EE) is shown in Figure 1.

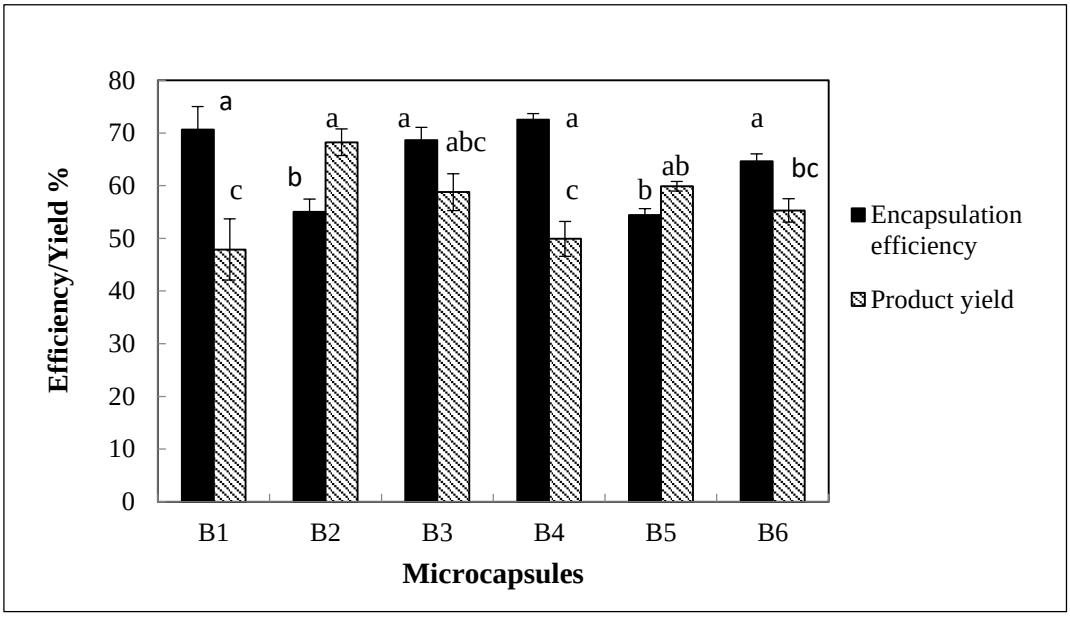


Figure 1. Encapsulation efficiency and encapsulation (product) yield of the microcapsules

The encapsulation yield changed between 47.89 % to 68.24 % according to the emulsion compositions. As the maltodextrin concentration increased in the feed emulsions, encapsulation yield significantly (P <0.05) increased. The decrease in EY percentage was reasoned by stickiness during spray drying. It was observed that some part of the emulsions stuck on the dryer walls during spray drying. Stickiness during spray drying depends on the surface temperature, water content and glass transition temperatures of the dried product (De Oliveira et al., 2009). Glass transition temperatures of maltodextrin DE 12 and gum arabic are 164°C and 102 °C, respectively (Roos and Karel, 1991). Present stickiness phenomenon in spray drying process can be explained by lower glass transition temperature of gum arabic than that of maltodextrin. A few degrees above the glass transition temperature, the particle surface reaches rubbery state and the particles begin to collapse. So, the encapsulation yield of B1 emulsion (AG:MD, 100:0) was significantly lower than other emulsions.

Moreover, the higher viscosity could affect the later formation of the dry surface and so the higher percentage of feed solids could stick on the dryer wall (Goula and Adamopoulos, 2004).

Encapsulation efficiencies of emulsions were determined in range of 54 % to 72 % depending on the emulsion composition. The highest efficiency of microcapsules was obtained from the emulsion prepared with 75:25 AG:MD. Similarly, in many researches stated gum arabic mixtures with maltodextrin and modified starch provided better encapsulation efficiency than pure gum arabic (De Araujo Santiago et al., 2016; De Barros et al., 2014; Przybysz et al., 2016).

The differences in encapsulation efficiencies can also be related to the emulsion viscosity. Emulsion viscosity is higher in pure gum arabic than gum arabic -maltodextrin mixtures. So, the crust formation is happened in a shorter time and resulted in higher retention of components. (Jafari et al., 2008).

Moisture content and water activity

The moisture content and water activity values of the microcapsules were given in Table 4. They changed between 1.91-2.83 % , and 0.120-0.145, respectively. The moisture content and water activity values were related to the drying operation conditions, such as inlet temperature and outlet temperature (Nadeem et al., 2011). The moisture content of dried product is also relevant to the temperature and humidity of the air leaving the drying process (Goula and Adamopoulos, 2008). In the present study, both inlet and outlet air temperatures were maintained at as possible as constant temperatures for obtain identical moisture content in all samples. The temperatures were constant and set by changing the flow rate of the feed emulsion during the drying processes. As a result, moisture content and water activities of the samples did not vary significantly (P >0.05).

Table 4 Moisture content and water activity of different ratio combinations of arabic gum and maltodextrin.

Wall material (AG:MD)	Moisture content (mL/100 g)	Water activity (a_w)
100:0	2.71 ± 0.21*[a]	0.145 ± 0.01*[a]
0:100	2.82 ± 0.16[a]	0.130 ± 0.03[a]
25:75	1.91 ± 0.25[a]	0.120 ± 0.02[a]
75:25	2.83 ± 0.49[a]	0.123 ± 0.02[a]
40:60	2.39 ± 0.38[a]	0.138 ± 0.01[a]
60:40	2.55 ± 0.58[a]	0.134 ± 0.01[a]

* The values are given in mean ± standard errors.(n=3)
Different superscripts letters in each column indicate statistical differences (P<0.05).

Bulk density and particle size distributions

Bulk densities of the powders varied significantly (P <0.01) between 364 kg/m^3 to 417 kg/m^3 according to the emulsion composition (Table 5). Bulk density increased significantly as the concentration of the gum arabic increased in the emulsions. Conversely, when the ratio of maltodextrin increased, bulk density decreased significantly (P <0.01). Thus, the highest bulk density obtained when the ratio of AG:MD was 100:0 (w/w) in the feed emulsion. This could be related to feed composition. When gum arabic was used, the viscosity of feed emulsion increased due to the higher viscosity effect of gum arabic. Higher infeed viscosity increased the feed rate to obtain a constant outlet temperature. At the higher feed rate, the shorter time required for particle film formation and this situation could affect the powder properties (Goula and Adamopoulos, 2004). When the feed flow rate increased, particle size of the microcapsules decreased, thereby bulk density of the powder increased.

Table 5 Bulk density and particle size characteristics of the essential oil microcapsules produced with gum arabic and maltodextrin

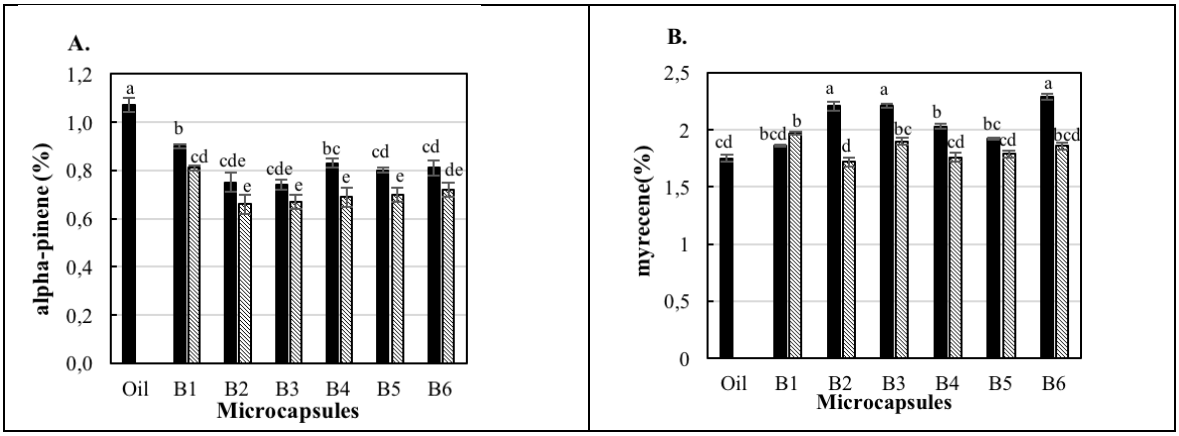
Wall material (AG:MD)	Bulk density (kg/m^3)	D50(μm)	D90(μm)
100:0	$417.7^{a} \pm 10.36^{*}$	$8.87^{a} \pm 0.07$	$23.19^{a} \pm 0.99$
0:100	$364.6^{c} \pm 4.1$	$7.65^{c} \pm 0.24$	$16.51^{c} \pm 0.66$
25:75	$380.9^{c} \pm 10.76$	$7.85^{bc} \pm 0.31$	$17.94^{c} \pm 0.78$
75:25	$382.32^{bc} \pm 2.41$	$8.51^{ab} \pm 0.16$	$22.09^{ab} \pm 0.66$
40:60	$378.7^{c} \pm 4.31$	$8.14^{abc} \pm 0.11$	$19.43^{bc} \pm 0.35$
60:40	$403.53^{ab} \pm 5.22$	$8.71^{a} \pm 0.39$	$22.83^{ab} \pm 2.24$

* The values are mean ± standard errors (n=3)
Different superscripts letters in each column indicate statistical differences *(P<0.01).

Table 5 also shows the particle size distribution of the powder particles. The particles' median diameters (D0,5) were changed between 7.65 and 8.87μm. Particles size increased when only gum arabic was used in the emulsion. When the bulk density and particle size results were compared, unlike expected, there was no such a negative correlation between bulk density and particle size. This can be related to hygroscopic properties of gum arabic. Indeed, gum arabic is more hygroscopic than maltodextrin. The powders produced with gum arabic were more hygroscopic so that these powders became damp and the particles grew. Thus, Jaya and Das (2004) used maltodextrin to overcome the stickiness problem of the mango powder and to get less hygroscopic powder. Feed flow rate could also be a reason of the stickiness problem. Higher feed flow rate can cause collision of small droplets and so the particle size of dried particles could be increased (Al-Asheh et al., 2003; Wang et al.,2015).

Effect of wall material composition on the retention of major essential oil compounds in microcapsules after storage

The important monoterpenes (α-pinene, myrecene, limonene, γ-terpinene, linalool, α–terpineol, geranyl acetate) composition of the essential oil recovered from the microcapsule were analysed after 20 days of the storage at 25°C. The results estimated in the % area of the components in GC chromatograms of the samples are shown in Figure 2. It can be clearly seen that there were losses of some components during the spray drying process. The losses of the volatiles during the spray-drying process can be explained by selective diffusion theory relevant to selective permeability. The theory presumed that the retention of the compound in the atomized drop is related to the relative volatility of the compounds (Bertolini et al., 2001).



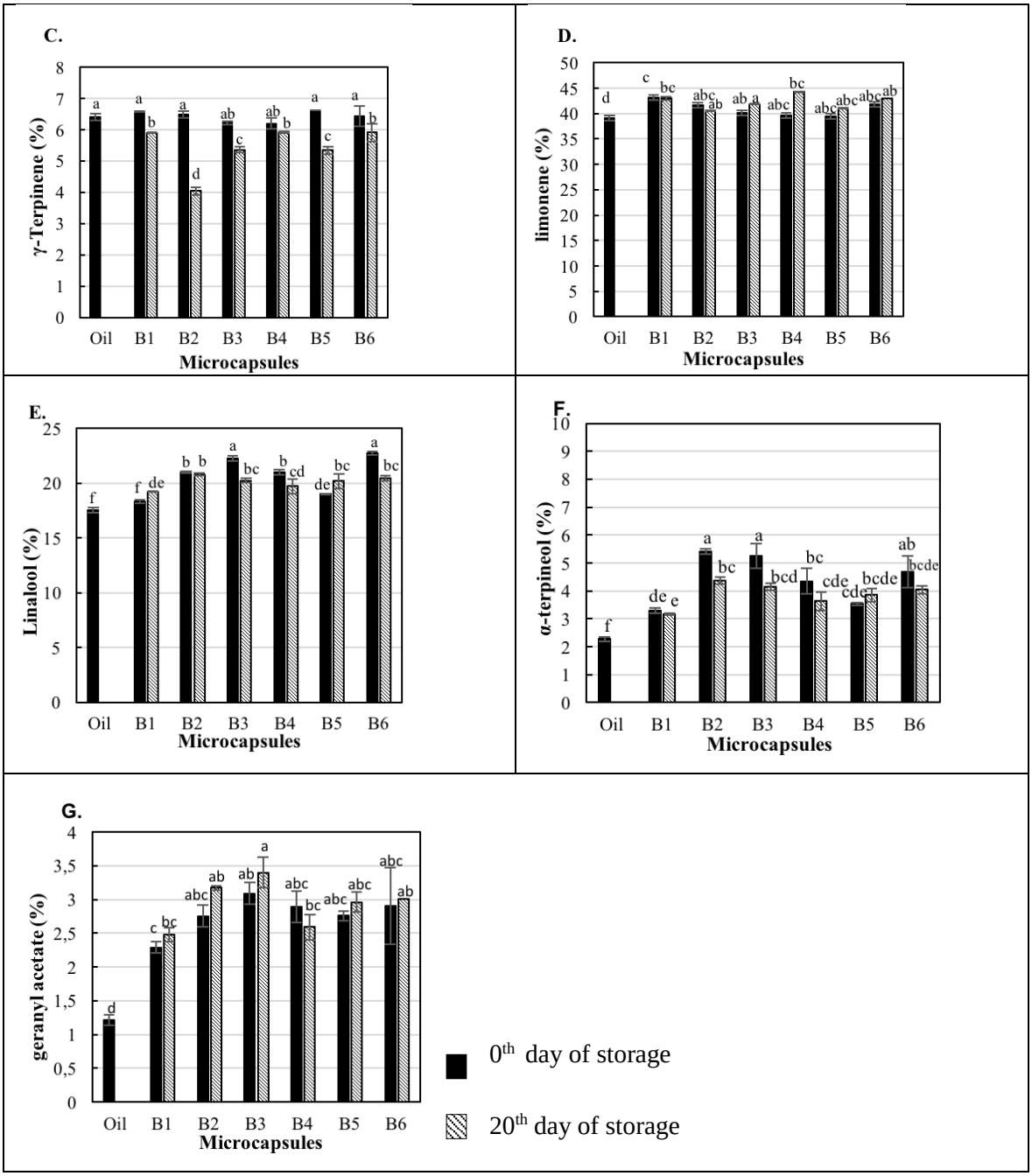


Figure 2. Main components in essential oil recovered from the microcapsules at 0th day and 20th day of storage (A. alpha-pinene; B.myrecene; C. γ-Terpinene; D.limonene; E.linalool; F. α-terpineol; G.geranyl acetate).

Emulsion compositions and storage had significant effects on the percentage of α-pinene in the microcapsules (Fig. 2A). The greater stability of α-pinene in both encapsulation process and storage was detected in samples produced with only gum arabic.

According to the results, myrecene percentage significantly increased (P <0.05) in all

microcapsules except produced with only gum arabic (B1 microcapsules) and 40:60 AG:MD microcapsules (Fig. 2B). Besides, myrecene percentage decreased significantly after 20 days of storage excluding microcapsules produced by gum arabic. Myrecene content not significantly changed in microcapsules produced with higher amount of gum arabic. The slight increase in myrecene percentage in some microcapsules could be related with linalyl acetate conversion in to β-myrecene by the elimination of acetate group at high temperatures (200 ^{o}C) during the drying process.

It can be observed in Fig. 2C that the percentage of γ-Terpinene did not significantly ($P > 0.01$) changed after the encapsulation. Emulsion composition also did not affect to the stability of γ-Terpinene in the microcapsules. However, wall material composition in the emulsion had a significant effect on γ-Terpinene retention during the storage. Retention of γ-Terpinene increased as the level of gum arabic was increased in the emulsions. Just like the myrecene, the lowest γ-Terpinene retention was detected in the microcapsules produced with only maltodextrin.

Limonene was the main component of the bergamot essential oil and its percentage was 40.92. (Fig. 2D) Limonene also did not significantly affect by emulsion composition and storage period of the microcapsules ($P > 0.01$). This could be related to its high boiling point (175-176 ^{o}C) so its volatility is lower than the other components.

As shown in Fig. 2E, percentage of linalool increased significantly in the microcapsules produced by all emulsions except B1 ($P < 0.05$). From these results, it was evident that gum arabic provided best protection of linalool than maltodextrin alone and the gum arabic and maltodextrin blends. Increment of linalool percentage in the microcapsules could be related with releasing of other minor components during the drying process. In terms of the essential oil components, there was no significant difference among the microcapsules produced with the gum arabic and maltodextrin mixtures after 20 days' storage ($P > 0.05$). However, linalool percentage increased significantly ($P<0.05$) in the microcapsules produced by AG:MD 100:0 and 40:60 blends while it decreased significantly ($P<0.05$) in 25:75, 75:25 and 60:40 blends.
In Fig. 2F, it was shown that the percentage of α-terpineol increased significantly after the encapsulation. The increment of α-terpineol could be related to high volatility of the other components during drying process. Indeed, the boiling point of α-terpineol is higher (219°C) than that of others major components.

Geranyl acetate percentage increased significantly after the encapsulation of oil in all microcapsules (Fig. 2G). This could be related with thermal degradation of linalyl acetate during the drying and distillation processes. Linalyl acetate undergoes thermal degradation in the presence of water leading to linalyl, geranyl, and neryl carbocation, which induce considerable rearrangement reactions as Babu and Singh (2010) reported. Thus, the percentage of neryl acetate and geranyl acetate were dramatically higher in the microcapsules.

Encapsulation process had minor effects on most of components in bergamot essential oil while it had major effect for some of them, during the process and storage depending on wall material compositions. As a result, a mixture of AG:MD could be suggested as a good wall material for encapsulation of bergamot essential oil encapsulation which could result better for protection of essential oil components against thermal degradations and oxidation effects during the drying process and storage.

CONCLUSION

In this study, different combinations of gum arabic and maltodextrin were evaluated in the microencapsulation of bergamot essential oil by spray drying. All the obtained powders had almost same moisture contents and water activity values. The encapsulation yield and efficiency were significantly affected by the wall materials composition. Although there is no statistical differences between encapsulation efficiencies of B1, B3, B4 and B6 microcapsules, the AG:MD

blend at the ratio of 75:25 (B4) provided the highest value (72.57%). Findings suggested that bergamot essential oil can be encapsulated without thermal degradation, oxidation reactions and releasing of components from powders. As a result, a new food-flavouring ingredient in powder form was produced successfully for using in many food formulations such as bakery, cake, salad dressings and beverages.

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