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Effect of Emulsifiers and Wall Materials on Particle Size Distribution and Stability of the Blended Essential Oils Nanoemulsions

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Abstract: In the present work, microencapsulation of the essential oil blend (clove + lemon peel + thyme) was successfully used to produce a product that can be used as food additives or in the pharmaceutical industry for the manufacture of a food supplement or so-called nutraceutical of plant origin. The characterization of the powder of the microcapsules made it possible to observe that the essential oil was successfully incorporated into the coating matrix. This was designed by the wall material, namely maltodextrin represented a barrier allowing the protection of the active principle, the control of its release and the property retention of the encapsulated essential oil for a long time. This powder of microcapsules of essential oil mixture can be successfully used for medical purposes to remedy certain pathologies, in particular for its antioxidant, antibacterial and anti-inflammatory properties.

Keywords: Clove (*Syzygium aromaticum*), thyme (*Thymus vulgaris* L.), lemon peel (*Citrus limon* L.), essential oil mixture, microencapsulation

1. Introduction

Essential oils are mixture of bioactive volatile constituents and they are benefit in many fields as pharmaceutical, flavor, perfume, food, agriculture, and detergent [1]. The great problem of these volatile constituents is their fragility and instability [2]. As a result, the degradation of the volatile oils is very quick by many unfavorable conditions as oxidation, volatilization, heating, and light. Such protection could provide a controlled release, thus increasing their action duration [3]. Encapsulation is the solution to solve this problem [4,5]. Constituents are bordered by covering materials that reduce the reaction between constituents and external factors as well as the costs of storage and transportation [6]. Encapsulation can modify the physical characteristics of the original product to facilitate its carriage, helps separate components of the mixture that otherwise react with each other, and provide adequate concentration and uniform dispersion of an active agent [7]. The technique of microencapsulation by atomization can maintain the main chemical compounds of these essential oils microencapsulated and made it possible to maintain their antioxidant and antimicrobial action against certain strains of pathogenic bacteria [8-10]. Likewise, this technique has made it possible to protect the volatile compounds of essential oils which are not stable and which can be oxidized and deteriorated when exposed to high temperature, oxygen, and humidity. This guaranteed protection of the microencapsulated active molecule until it reaches its site of action [9]. This study aimed to highlight the effect of different microencapsulation parameters on encapsulation effectiveness of essential oil mixture from clove, lemon peel and thyme.

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2. Materials and Methods

2.1 Plant Material

Clove (*Syzygium aromaticum*), thyme (*Thymus vulgaris* L.) and lemon peel (*Citrus limon* L.) were selected as plant material for this study. Clove was purchased from the market in the form of dried flower buds. Thyme was collected in March from the mountain of Bou Garnine. Lemon peel was obtained from the lemon tree variety 'Eureka'.

2.2 Essential Oil Extraction

The essential oil of thyme and lemon was determined by Clevenger apparatus while clove essential oil was obtained by hydrodistillation.

2.3 Microencapsulation Procedure

(a) Formulation of the Nanoemulsion Based on Optimized Blended Essential Oils

A mixture was spray dried (Table 1). Prior to microencapsulation, each encapsulating agent was dispersed in distilled water and stored in the refrigerator for 12h for complete hydration. Then the mixtures were added and mixed with an IKA brand Turrax homogenizer (IKA, Delaware, USA) at 10,000 rpm for 5 min. Once the mixture had been made, it was introduced into the BUCHI mini-B-290 spray dryer (BUCHI, Flawil, Switzerland) [11].

Table 1 - Mixture prepared for micro-encapsulation of essential oil mixture

EO	Tween 20	Conservator	Water	Maltodextrin
0.5 %	0.5 %	0.6 %	1 L	5 %

EO: Essential oil

(b) Spray Drying Procedure

A BUCHI mini-B-290 laboratory atomizer (BUCHI, Flawil, Switzerland) with a standard 0.5 mm nozzle was used following the method of Chatterjee and Bhattacharjee [10]. The spray drying was determined with Equation 1:

$$\text{Spray drying yield (\%)} = \frac{\text{Mass of final product (g)}}{\text{Total amount of solid introduced (g)}} \text{ X } 100 \quad (1)$$

2.4 Physicochemical Characterization of the Active Nanoemulsion

(a) Microcapsule Size

The size of the particles can be determined by the determination of particle movement in a fluid of known temperature and viscosity. This analysis was carried out with a Zetasizer Nano-ZS/Malvern Instruments, United Kingdom.

(b) Nanoemulsion Stability Evaluation

Also, the zeta potential is the measure of the intensity of the electrostatic or electrical repulsion/attraction between particles [12].

2.5 Characterization of the Final Product

(a) Optical Observation of Microcapsules

Optical observations of the microcapsules were made using an optical microscope (Bioval L-2000A) attached to a digital camera. The size distribution of microcapsules was assessed [13].

(b) Physicochemical Characterization

The water solubility (SI) was determined according to Navarro-Flores *et al.* [11] and Fernandes *et al.* [14]. SI and swelling capacity (SC) were calculated by using the following equations:

$$\text{SI (\%)} = \frac{\text{Weight of the dried supernatant}}{\text{Initial weight of microcapsules}} \text{ X } 100 \quad (2)$$

$$\text{SC (g/g)} = \frac{\text{Weight of the dried supernatant}}{\text{Initial weight of microcapsules (100 - SI)}} \text{ X } 100 \quad (3)$$

The hygroscopicity and wettability of essential oil microcapsules was determined according to the method of Fernandes *et al.* [14]. The density of essential oil microcapsules was determined according to Ramakrishnan *et al.* [15]. The essential oil encapsulation retention (%) was determined following Tomazelli *et al.* [8] and it was calculated using Equation 4. The essential oil encapsulation efficiency (EE) was calculated using Equation 5 [14] and following the method of Tomazelli *et al.* [8]. The antioxidant activity of microencapsulated essential oil was determined according to the radical inhibition of DPPH (%) for 1 mg of sample (Equation 6) [16]. Meanwhile, the essential oil composition before and after microencapsulation was determined using a Varian CP-3800 gas chromatograph equipped with a CP-Sil 8 CB Low Bleed/MS column (30 m × 0.25 mm). The equipment conditions were set by Leimann *et al.* [13].

$$\text{Essential oil retention (\%)} = \frac{\text{Total essential oil in powder}}{\text{Initial essential oil (dry basis)}} \text{ X } 100 \quad (4)$$

$$\text{Essential oil encapsulation efficiency (\%)} = \frac{\text{Total essential oil} - \text{Surface essential oil}}{\text{Total essential oil}} \text{ X } 100 \quad (5)$$

$$\text{Inhibition percentage (\%)} = \frac{\text{DO control} - \text{DO sample}}{\text{DO control}} \text{ X } 100 \quad (6)$$

2.6 Statistical Data Processing

All analyzes were done in three replicates and the comparison of the means was carried out by Analysis of Variance (ANOVA). Duncan's multi-range test was used at the significance level of 0.05.

3. Results and Discussion

3.1 Optimization of the Particle Size Distribution and Stability Properties of the Active Nanoemulsion

(a) Effects of Emulsifiers and Wall material Types on the Particle Size Distribution

In terms of particle size, the obtained results given by Fig. 1 shows that Tween 20 allowed us to obtain a better particle size of encapsulated blend essential oil into the emulsion with 143.2 nm, compared to Tween 40 (346.30 nm) and Tween 80 (183.2 nm). However, it turned out that maltodextrin is the best type of coating support because it allowed us to obtain encapsulated oil particles of small size of the order of 134.37 nm compared to that gum Arabic (323.77 nm) and casein (406.57 nm). Rosemary essential oil encapsulated with maltodextrin and Tween 20 revealed an average diameter particle size of 256.56 nm [17]. Esmaeili and Asgari [18] had used *Carum copticum* essential oil to prepare the ionic gelation process and found that nanoparticles had an average diameter of 236-721 nm.

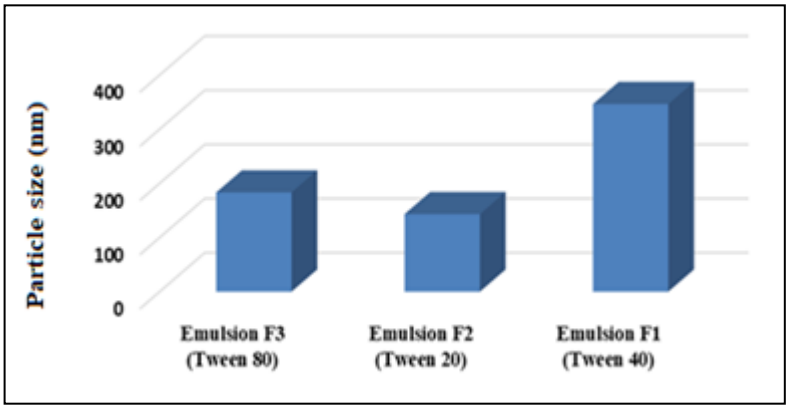

Fig. 1 - Evaluation of the size of the essential oil particles in the formulated emulsion against different types of surfactants

(b) Effects of Emulsifiers and Wall Material Types on the Stability Properties

The obtained results of the stability analysis given by Fig. 2 shows that Tween 20 was considered as the best surfactant with the best emulsifying power because it makes it possible to obtain the most stable emulsion with a zeta potential furthest from zero 0 mV which of the order of -26.5 mV which is high relative to the zeta potential of the Tween 40 (-25.33 mV) and Tween 80 (-23.93 mV) emulsifiers. Also, according to our results as well as the results of some recent work, it turned out that the low molecular weight (1225 Daltons), the value of the hydrophilic-lipophilic balance (HLB) (equal to 16.7; characterizing a molecule completely hydrophilic) and the nature of the electric charge

(nonionic surfactant) of the surfactant used (Tween 20) showed a great impact on the size of the particles as well as the stability of the nanoemulsion which is of the oil-in-water type (O/W) [19,20].

In addition, the stability analysis made it possible to observe that the use of maltodextrin as coating support made it possible to obtain an emulsion of considerable stability having a zeta potential of the order of -27.3 mV which makes it possible further from zero 0mV and higher compared to other materials such as gum Arabic (-19.77 mV) and casein (-14.73 mV). Indeed, these results are consolidated by the criteria of the stability of an emulsion which have been defined by the literature, which shows that the zeta potential is considered as a useful parameter to predict the stability of the dispersion by measuring the surface charge droplets. In addition, they had shown that to ensure the physical stability of a nanoemulsion, the value of the zeta potential must be far from zero, greater than 30 mV or less than -30 mV [21].

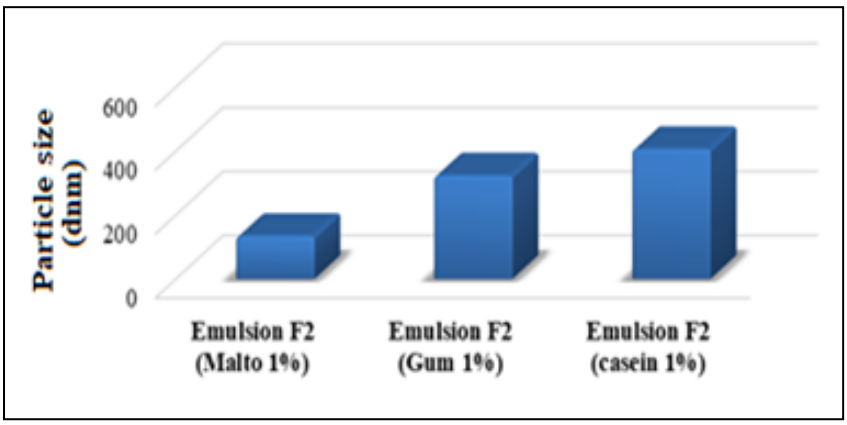

Fig. 2 - Evaluation of the size of microencapsulated essential oil particles with respect to the different types of bio-based coating materials

According to our results maltodextrin which was used as a wall material to encapsulate essential oil showed a considerable influence on the particle size as well as the stability of the emulsion [19]. On the other hand, according to previous work, this coating material alone has no effect on the stability of the emulsion because it did not have any surfactant sites to be adsorbed on the emulsion droplet. Moreover, in the presence of emulsifier or surfactant (such as tween 20 in our case) was inevitable to obtain long-term stability of the nanoemulsion [19]. Indeed, the surfactant stabilized the emulsion by inserting its non-polar tail into a helical coil of maltodextrin to adsorb onto the droplet and reduce the surface tension at the interface [21,22].

3.2 Microencapsulation Yield of Essential Oil Microcapsule Powder

The microencapsulation yield of the essential oil mixture obtained by spray drying is 67.378% (Fig. 3). Previous work, by Gouin, [23] and Yeo *et al.*, [24] have shown that microencapsulation by spray drying can lead to yields which can reach up to 40-50 %. This yield is very low compared to that obtained in our case which proves the effectiveness of the microencapsulation process. This result was related to the optimization of the spray drying process by the reliable adjustment of the spray dryer parameters such as the inlet and outlet air temperature, the supply flow of the solution to be dried, the atomizing air flow rate and the vacuum gas flow rate, in order to maintain the homogeneity of the solution.

Fig. 3 - Microcapsule powder of essential oil mixture obtained by spray drying

3.3 Optical Observations of the Prepared EO Microcapsule Powder

Analysis of optical observations of essential oil microcapsules powder formulated by the blend essential oil which were performed using a light microscope (Fig. 4) shows a clear and homogeneous distribution of the EO microcapsule with the same spherical shape. This result proves a good and effectiveness microencapsulation process. Similar results were obtained by Banasaz *et al.* [25] who shown that a similar appearance was found depending on the choice of the suitable surfactant in the nanoemulsion types. Following the optimization of the technique of micro-encapsulation of essential oils, a physicochemical characterization of the microencapsulated essential oil powder was developed, and the results obtained made it possible to identify certain criteria of the final products.

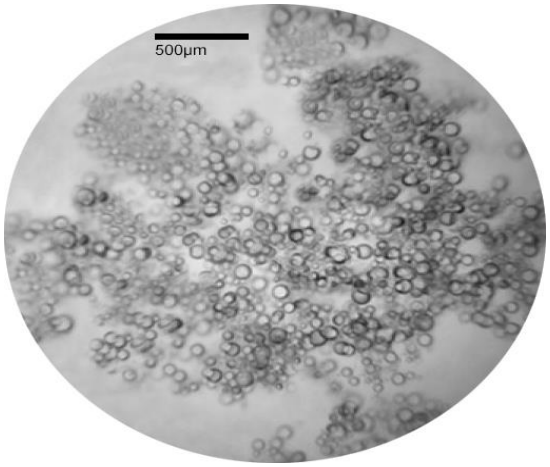

Fig. 4 - Optical observations of essential oil microcapsules

3.4 Physicochemical Characterization of the Essential Oil Microcapsule Powder

In our present study, the permeability and rehydration properties of microcapsules were evaluated in terms of water solubility index (SI), swelling capacity (SC), hygroscopicity (HY) and wettability (W) compared to that of the encapsulating agent.

(a) Water Solubility Index (SI)

The results obtained following the characterization of the essential oil microcapsule powder showed that the water solubility index (SI) was between 85.93 ± 0.570 for MT + EO and 92.98 ± 0.617 % for MT (Table 2). Different results were obtained by Fernandes *et al.* [14] in the case of Brazilian rosemary essential oil microencapsulation. It was found that despite the hydrophobic character of the encapsulation, the high solubility of the microcapsules could be due to the fact that the encapsulating agent (maltodextrin) had a high solubility in water and that is why it was mainly used in the drying process, promoting the solubility of microencapsulated essential oil [26].

(b) Swelling Capacity (SC)

In contrast, the essential oil microcapsule powder was characterized by a swelling capacity (SC) which is of the order of 11.074 ± 0.07 g/g (MT + EO) (Table 2) slightly low by compared to that of the wall material which is maltodextrin of the order of 13.252 ± 0.08 g/g (MT). This variation is not significant (P value> 0.05) so this microencapsulation promotes the passage of the essential oil in its encapsulated form through the gastrointestinal barrier. Lower values of SC (2 and 3 g/g) were obtained by Paini *et al.* [27] in the microencapsulation of phenolic compounds from olive pomace. Swelling studies revealed that the penetration of water into the interior of the microcapsule was strongly influenced by the nature of the encapsulating material as well as the nature of the encapsulate [11].

(c) Hygroscopicity (HY)

The hygroscopicity (HY) (Table 2) of the EO microcapsule powder was found to vary from 16.09 ± 0.106 for MT + EO to 19.98 ± 0.132 % for MT. A slight decrease in the hygroscopicity of the coating material is closely related to the hydrophobic nature of the essential oil (the encapsulant). Indeed, according to Frascareli *et al.* [28], a similar behavior was found for coffee oil microencapsulation by spray drying with hygroscopicity values varying between 13.73 % and 17.89 % and this using gum Arabic as an encapsulant. Similarly, Fernandes *et al.* [29] by increasing the load of rosemary essential oil in the emulsion, the particles obtained exhibited a lower hygroscopicity varying between 9.3 % and 13.9 % due to the nature hydrophobic of the essential oil itself, which does not absorb water. The lowest

hygroscopicity values were found in high concentrations of wall material. This demonstrates the effectiveness of maltodextrin and modified starch as carrier agents in the treatment of materials with low values of hygroscopicity [30,31].

(d) Wettability

The results obtained show that the microcapsule powder has a wettability (MH) (rehydration capacity in water) of the order of 212.99 ± 1.41 seconds for the essential oil coated with wall material which is maltodextrin (MT + EO) which slightly less than that of varied from 151.99 ± 1.009 seconds for maltodextrin only (MT) (Table 2). This slight difference cannot affect the crossing of the active molecules of the essential oil, the two successive barriers corresponding to two stages:

i. Penetration passage of an active molecule from the external environment into the interstitial fluid.
ii. Resorption passage of an active molecule from the interstitial fluid to the circulating fluid.

In addition, according to the literature, values close to these were found by Fernandes *et al.*, [14] which demonstrated the wettability of the rosemary essential oil microcapsule powder and which required a wettability time. of the order of 155 seconds. Indeed, this proves that the capacity of microcapsules to absorb water is directly affected by the hydrophobicity of the encapsulated product (EO) and by the molecular interaction between the two phases in the nano-emulsion [32]. This parameter also depends on particle size, density, porosity, and the presence of amphipathic substances on the surface [29].

Table 2 - Physicochemical and antioxidant characterization of microencapsulated essential oil powder

	PI (%)	SI (%)	SC (g/g)	HY (%)	W (Sec)	R_{HE} (%)	EE (%	D (g/ml)
MT	-	92.98±0.617	13.252±0.08	19.98±0.132	151.99±1.009	-	-	0.202±0.001
MT+HE	64.08±0.425	85.93±0.570	11.074±0.07	16.09±0.106	212.99±1.41	64.997±0.431	76.15±0.506	0.224±0.001

IP: Inhibition percentage; IS: Solubility index in water; SC: Swelling capacity; HY: Hygroscopicity; W: Wettability; R_{HE}: Essential oil retention EE (%): Efficiency of essential oil encapsulation and D: Density

3.5 Essential Oil Retention and Microencapsulation Efficiency

(a) Essential Oil Retention

Following the characterization of the microcapsule powder of the essential oil mixture, we found that the retention of the essential oil is of the order of 64.997 ± 0.431 % (Table 2). According to the literature, it has been shown that the nature of the wall material as well as the chemical characteristics of the bioactive substance retained can influence this parameter. In addition, similar results were found by Tomazelli *et al.* [8] in the microencapsulation of thyme essential oil by spray drying using maltodextrin as coating material expressed essential oil retention of 57.37 %. Likewise, a result in accordance with ours was found by Fernandes *et al.* [29] in rosemary microencapsulation by spray drying which evaluated the effects of gum Arabic on the degree and efficiency of EO trapping during micro-encapsulation (Table 3).

Table 3 - Chemical composition of essential oils by gas chromatography (GC) before and after microencapsulation

Composés volatiles	(%)			
		Before micro-encapsulation	After micro-encapsulation	
	Retention time	EO pure mixture	EO superficial	EO after total release
α–Pinene	5.433	0.549±0.041	-	0.479±0.008
β –Pinene	6.343	2.231±0.054	-	1.95±0.031
β -Myrcene	6.663	0.434±0.056	-	0.38±0.006
Limonene	7.617	22.373±3.465	2.719±0.044	19.554±0.314
p-Cymene	11.099	3.776±0.058	0.434±0.007	3.3±0.053
beta.-Phellandrene	11.238	0.422±0.058	0±0	0.369±0.006
γ–Terpinene	8.228	3.036±0.064	0.375±0.006	2.653±0.043
α -Terpineol	11.43	0.446±0.008	-	0.39±0.006
Z-Citral	12.488	0.964±0.632	-	0.843±0.014
E-Citral	13.181	1.15±0.111	-	1.004±0.016
endo-Borneol	15.713	0.642±0.082	-	0.56±0.009
4-Terpineol	16.099	0.386±0.084	-	0.337±0.005
Caryophyllene	16.437	0.707±0.184	-	0.617±0.01
Thymol	19.546	26.781±1.622	3.344±0.054	23.407±0.376
trans-Caryophyllene	22.868	1.048±0.119	-	0.915±0.015
Eugenol	25.15	33.987±1.25	4.243±0.068	29.705±0.477
Acetyleugenol	30.173	1.07±0.885	-	0.935±0.015

(b) Microencapsulation Efficiency

It was found that the obtained essential oil microcapsule powders were characterized by a considerable microencapsulation efficiency of 76.15 ± 0.506 % (Table 2). Similar results have been found by Tomazelli *et al.* [8], which showed that thyme essential oil microcapsule powder obtained by spray drying and using maltodextrin as the wall material exhibited microencapsulation efficiency (87.16 %). It can then be seen that the optimized essential oil mixture based on a mixture of oils obtained from these three species of aromatic and medicinal plant, namely the clove (*Syzygium aromaticum*), the lemon tree (*Citrus limon* L.) and common thyme (*Thymus vulgaris* L.) has been successfully encapsulated in the coating matrix represents a barrier allowing the protection of this active principle by protecting it against any kind of degradation by oxidation until its release at their site of action.

(c) Microencapsulation Density

An evaluation of the density of the microencapsulated EO powder showed a slight increase in the density of the microencapsulated oil powder, which was detected, this variation may be related to the hydrophobic nature of the encapsulated essential oil mixture that occupies a large space in the particles and under the envelope. However, recent work by Tonon *et al.* [32] and Fernandes *et al.* [13] had shown that the bulk density of rosemary essential oil microcapsules increased as a function of the high concentration of the encapsulate. This was because the hydrophobic and heavier material fits more easily into the spaces between the particles, resulting in a higher density.

3.6 Antioxidant Activity of Microencapsulated Essential Oil

A study leading to the evaluation of the antioxidant activity of microencapsulated essential oil showed that the resulting microcapsule powder exhibits considerable antioxidant activity. This antioxidant activity was lower than the results reported in the literature for encapsulated clove essential oil. Indeed, Sebaaly *et al.* [34] obtained an inhibition of the higher free radical DPPH ranging from 89.3 to 92.31 % for the essential oil of clove encapsulated in cyclodextrin. This result was probably due to the nature of the wall material used during the microencapsulation, which has different properties, including their release power, allowing better conservation of bioactive compounds, protection against oxidation and more great release of the compounds presented in the essential oil at their site of action. Likewise, Meneses *et al.* [35] found that the inhibition of free radical DPPH was greater than 80 % for the essential oil of clove encapsulated in lipids. These differences in antioxidant activity may be related not only to wall materials, but also to particle characteristics such as size and charge, and the analytical method employed (Table 2).

3.7 Chromatographic Profile of the Release of Active Compounds from Microencapsulated Blend EO

After obtaining the powder by microencapsulation of the essential oil mixture, the microcapsules were washed with solvent and extracted by hydrodistillation in order to verify by gas chromatography coupled with mass spectrometry, first of all, the presence of any trace of volatile compounds collected by the solvent from the surface of the capsules and secondly to compare the composition of the EO before and after microencapsulation. The identified compounds are listed in Table 3. Chromatographic analysis showed the presence of some compounds on the surface of the microcapsules which escape from the envelope and which are on the trace scale such as limonene, *p*-cymene, γ -terpinene, thymol and eugenol having the following contents 2.71 ± 0.044 %; 0.434 ± 0.007 %; 0.375 ± 0.006 %; 3.344 ± 0.054 % and 4.243 ± 0.068 % respectively (Table 3).

Likewise, the chromatographic analysis of the essential oil (obtained after microencapsulation) which was obtained after extraction or total release from the microcapsules by hydrodistillation showed the presence of seventeen major volatile compounds, the main ones of which are represented by β-pinene (1.95 ± 0.031 %); limonene (19.554 ± 0.314 %); *p*-cymene (3.3 ± 0.053 %): γ -terpinene (2.653 ± 0.043 %); thymol (23.407 ± 0.376 %) and eugenol (29.705 ± 0.477 %) (Table 3).

To ensure the effectiveness of microencapsulation by the spray drying technique, a chromatographic analysis of the essential oil (obtained after microencapsulation) was developed and the results proved that the essential oil removed from the microcapsules retained its total chemical composition compared to that of pure essential oil (obtained before microencapsulation) with a slight variation in the concentration of certain volatile compounds due to slight degradation during the encapsulation process (Table 3). This showed that the formation of the microcapsules made it possible to preserve the chemical and biological quality of the essential oil trapped in the capsules. This supports the hypothesis that these volatile compounds were preserved under the coating formed by the polymer and which is due essentially to the phenomenon of crosslinking which took place between the functional group of the volatile compounds and the maltodextrin forming the wall of the microcapsules. In addition, the microencapsulation process by spray drying and using maltodextrin as wall materials has shown its effectiveness for the conservation of the functional and biological properties of the active principle demonstrated. These results have been consolidated by the work of Tomazelli *et al.* [8] and Leimann [13].

4. Conclusion

This study shows the synthesis of clove, lemon peel and thyme essential oil microcapsules. In order to obtain the best microencapsulation formulation for clove, lemon peel and coriander essential oil, the influence of microencapsulation parameters on encapsulation efficiency and oil release rate was evaluated. The oil release rate evaluation suggests that the formation of the microcapsules made it possible to preserve the chemical and biological quality of the essential oil trapped in the capsules.

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