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ORIGINAL PAPER

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Properties of caraway (*Carum carvi* L.) essential oil encapsulated into milk protein-based matrices

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Abstract Encapsulating properties of whey protein concentrate (WPC), skimmed milk powder (SMP), and their mixtures with maltodextrins (MD) for encapsulation of caraway essential oil by spray drying were studied. Encapsulation efficiency (EE) was higher in WPC-based matrices compared to SMP. Partial replacement of WPC by various MD increased the retention of volatiles during spray drying and enhanced protective properties of solidified capsules against oxidation and release of volatiles during storage. The opposite tendency was shown by SMP matrices: adding MD to the wall composition resulted in lower retention of volatiles during drying and lower oxidation stability compared to the SMP and all WPC based matrices. Dynamic headspace analysis (DHS) was applied to determine the rate of release of volatiles from the microencapsulated powders. Results revealed that combined matrices of SMP and carbohydrates had the highest volatile release ratio. Partial replacement of WPC by MD significantly reduced release of volatiles from capsules as determined by DHS. Flavor profile of caraway oil entrapped in the matrix was similar to that of pure essential oil: a small decrease in limonene content was recorded for some matrices. The results of scanning electron microscopy (SEM) of microencapsulated particles showed WPC-based matrices to have less visible cracks and holes compared to SMP. More dented surfaces could be observed in particles containing MD as compared to WPC only. It was concluded that WPC-based matrices were more effective as caraway oil encapsulating agents as compared to those of SMP. The incorporation of carbohydrates to WPC results in obtaining more effective microencapsulants.

Keywords Encapsulation · Caraway essential oil · Milk proteins · Flavor release · SEM

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Introduction

Flavor compounds are rather volatile liquids and generally thermally or chemically labile in native. Microencapsulation has become an attractive approach to convert liquid food flavorings into a dry and free flowing powder form, which is easy to handle and incorporate into a dry food system [1]. The process is defined as a physical one where thin films or polymer coats are applied to small solid particles, droplets of liquids, or gases [2]. Besides the change of the physical characteristics of the original material, food flavors are encapsulated for several other reasons: (1) to retain them in a food product during storage; (2) to protect the flavor from undesirable interactions with the food; (3) to minimize flavor/flavor interactions within a mixture; (4) to guard against light, heat, moisture, or air induced reactions or oxidation; (5) to provide the controlled or delayed release of flavor; (6) to mask objectionable flavors [3]. Microencapsulation can be accomplished by different techniques: spray drying, spray chilling and spray cooling, extrusion, air suspension coating, multi-orifice centrifugal extrusion, coacervation/phase separations, liposome entrapment, inclusion complexion, co-crystallization, interfacial polymerization [1, 4, 5]. Spray drying remains the dominant method for encapsulating flavors due to a low cost and readily available equipment although there are several disadvantages to this method, e.g., loss of volatiles, degradation of sensitive compounds, and further need of fine powder processing such as agglomeration to instantize the dried material or make it more readily soluble [5, 6]. Leaflash spray drying modification has been proposed in which the drying air is of very high temperature (300–400 °C) and flows at a very high velocity [7]. It was found that citral and linalyl acetate could be spray dried with little impact on the compounds themselves.

Different coating materials have been used to produce microcapsules including gums, carbohydrates, celluloses, lipids, inorganic materials, and proteins. Carbohydrate based matrixes are dominating in flavor encapsulation [3, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19].

The main disadvantage of most carbohydrate coating materials is their low emulsifying capacity and marginal retention of volatiles. Functional properties of food proteins, i.e., solubility, viscosity, emulsification, film formation, the ability to interact with water, small ions and other polymers, groups at the oil/water interface allowing stabilization of emulsion droplets [20, 21, 22] exhibit many of the characteristics that are desired for a wall material. However, publications on the use of food proteins as coating materials for flavors are rather scanty. It was shown that proteins usually possess high binding capacity for flavor compounds [23, 24]. The flavor binding mechanism to proteins depends on the relationships between conformational states of proteins [25, 26, 27] and nature of aroma compounds [28, 29]. Special attention has been given to β-lactoglobulin, the most abundant protein in whey. Papiz et al. [30] postulated it to belong to the superfamily of proteins involved in the strong interactions with small hydrophobic molecules. Some studies were focused on the binding of selected flavor compounds such as aldehydes, ketones, esters, acids, pyrazines, aromatic compounds, or terpenes [27, 28, 31, 32, 33]. Hydrophobic interactions were found for ketones, esters and, alcohols and covalent or hydrogen bonding was found with aldehydes [27, 28, 32, 33, 34]. However, the data obtained often differ among the authors, due to different experimental conditions and methodologies used. Some investigations have proved milk proteins to function well for encapsulating anhydrous milk fat, soybean, palm based oils, and methyl linoleate [35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51]. Nevertheless, on the basis of the chemical and physicochemical properties of the investigated proteins, it is expected that they will be used as a wall material for flavor encapsulation via spray drying. To our knowledge, flavor encapsulation into protein based matrixes has been comparatively little investigated [52, 53, 54]. No reports were found on the microencapsulation of many less commercially important essential oils than those of citrus, mint, onion, and garlic. In 1996 the microencapsulation properties of gum arabic and several food proteins (whey protein isolate (WPI), soy protein isolate (SPI) and sodium caseinate (SC)) have been investigated [53, 54]. SPI was found to be the most effective matrix for retaining orange oil during spray-drying of the emulsions (effectiveness=85.7%), followed by SC (81.7%), gum arabic (GA) (75.9%), and WPI (72.2%). Scanning electron microscopy (SEM) and confocal scanning laser microscopy (CSLM) revealed that spray dried GA-microencapsulated orange oil particles had undergone more shrinkage during drying than the protein microencapsulated products.

This study aimed to investigate encapsulating properties of milk proteins and their mixtures with carbohydrates for encapsulation of caraway (*Carum carvi* L.) essential oil, which is one of the most popular flavorings in Lithuania and many other countries. Evaluation of effectiveness of encapsulation process, resistance to oxidation, flavor profile, and release by microencapsulated products, as well as the outer structure of spray dried particles, have been investigated.

Materials and methods

Materials. Whey protein concentrate (WPC) and skimmed milk powder (SMP) obtained from the local dairy; maltodextrins (MD): N-Lok (produced from waxy maize), Encaps-855 (produced from waxy maize), Capsul-E (produced from tapioca) obtained from National Starch & Chemical, U.S.A; corn starch (CS), modified starch (MS) Ctex 06205 (an acetylated distarch adipate on waxy maize starch) obtained from Cerestar; all were used as encapsulating agents. Caraway (*Carum carvi* L.) essential oil was purchased from the Frey+Lauhenstedtulzburg, Germany.

Emulsion preparation and drying. Solutions of coating matrixes, 30 wt% concentration, were prepared by reconstituting dried powders of WPC/SMP in 50 °C deionized water. Maltodextrins were added to protein matrixes in a ratio 1:9 after being dissolved at 80 °C. Solutions were allowed to cool to the room temperature and were being mixed overnight to enhance hydration. Caraway essential oil (15 wt% of matrix solids) was warmed to 40 °C and emulsified into the hydrated coating material. Homogenization was accomplished by Ultra Turrax Ika 25 basic homogenizer (Janke & Kunkel GmbH & Co.) operating at 20,000 rpm for 5 min. Emulsions were spray-dried in a Büchi 190 Mini Spray Dryer (Donau, Switzerland) under the following parameters: spray nozzle (inlet) temperature – 180±5 °C, outlet air temperature – 90±5 °C; pressure – 750–800 mm/H_2O. Dried products were packed into glass containers and stored in the laboratory freezer until evaluation.

Determination of total oil. The content of total oil retained after spray drying was determined by distilling 10 g of encapsulated dried powders for 3 h in a Clevenger-type apparatus (European Pharmacopoeia). The weight of oil recovered from the sample and collected in the trap was calculated by multiplying by a density factor of 0.88 g/ml. All samples were analyzed in triplicate.

Determination of surface oil. Surface oil was washed for 4 h from 10 g of powder in a Soxhlet extraction apparatus by using pentane. One ml of pentane containing 0.3 vol.% decane as internal standard was added to the obtained extract prior to evaporation under the nitrogen. Each extract was evaporated to a final volume of approximately 2 ml under a stream of nitrogen at room temperature. The amount of oil in the sample was determined by gas chromatography (GC) using Fisons 8000 series chromatograph with FID under the following conditions: fused silica capillary column DB 5 30 m length, 0.32 mm internal diameter, and 0.25 μm film thickness; helium as carrier gas with a linear velocity 35 cm s^{-1}; temperature programming from 50 °C with 5 min hold to 220 °C increasing at 4 °C min^{-1}; injector temperature 230 °C, detector 260 °C.

Determination of moisture. Moisture was determined by distillation from toluene. A 10-g sample of encapsulated caraway oil was refluxed with 100 ml toluene for 2.5 h in a boiling 250-ml flask fitted with a Biddable-Sterling trap and a water-cooled condenser. Volume of the collected water was read directly from the trap.

Evaluation of storage stability. Five grams of each spray-dried microencapsulated product was washed with pentane to remove their surface oil and placed in separate 40-ml bottles, tightly capped and stored at 50 °C in the dark and at room temperature in the absence and presence of light. For comparison, non-encapsulated caraway essential oil was simultaneously stored under the same conditions.

Samples for GC analysis were prepared according to the method of Risch and Reineccius (1988). A 0.15 g sample of powder was dissolved in 0.85 g distilled water. Then 4 ml of acetone containing 0.3 vol.% decane as internal standard (IS) was slowly add-

ed. Solutions were continuously shaken for 2 h, and afterwards the sample was allowed to settle and 1 µl liquid phase aliquot was injected into the GC for limonene oxide content analysis without further preparation. GC operating conditions were the same as described in the surface oil determination section.

Release of volatiles by dynamic headspace analysis (DHS). Five grams of the sample which had been extracted with pentane for surface oil determination were placed into a 200-ml sample flask and flushed for 30–240 min with nitrogen at a flow rate of 450 ml/min to recover the volatiles accumulated in the headspace during the timed interval. The volatiles trapped in 0.4 g Tenax, TA 35/60 mesh were desorbed by 15 ml of diethyl ether. After adding 1 ml of IS (0.3 vol.% decane in diethyl ether) to the desorbed volatiles, they were evaporated to a final volume of 1 ml under a stream of nitrogen and analyzed by GC under the conditions described above.

Scanning electron microscopy (SEM). A JEOL 840-A model scanning electron microscope was used to investigate the microstructure properties of spray-dried microencapsulated products. Specimens were coated with gold with the sputter coater Balzers SCD 004. The conditions to operate the electron microscope were as follows: working distance 39 mm, acceleration voltage 10 kV.

Results and discussion

Retention of volatiles and encapsulation efficiency

Nine constituents were identified in a fresh caraway essential oil: α-pinene, sabinene, myrcene, limonene, *cis*- and *trans* dihydrocarvone, carvone, dihydrocarveol, and β-caryophyllene. It is well known that caraway oil consists mainly of limonene and carvone. The first compound is a hydrocarbon, which is also the main constituent of citrus oils, the second one is a terpene ketone, which is an important constituent of such aromatic plants as spearmint [L(–)-carvone] and dill [D(+)-carvone]. The main characteristics (total retained oil, surface oil, effectiveness of encapsulation process, and moisture) of investigated spray-dried encapsulated products are given in Table 1. It should be noted that only traces of oil were hydrodistilled from CS and MS matrices after spray drying. Only a slight improvement was achieved by adding some MD to CS. Retention of oil in the MD was also low, up to 25% from the oil added to emulsion. The result shows that these matrixes at the parameters of emulsification used can retain only a small amount of essential oil. Reineccius [55] determined that emulsion particle size has a significant effect on the retention of orange oil in some carbohydrate matrixes: the coarser the emulsion (i.e., the larger the particle size), the poorer the flavor retention. Since MD and CS have no good emulsification properties, they produce coarse emulsions and therefore poor flavor retention during drying. Fine homogenization at the elevated pressures has not been applied to the preparation of emulsions in our study and this factor could be crucial to the losses of oil during spray drying. Because of the poor capacity to retain volatiles, the carbohydrate-based matrixes were not considered for further investigation.

Protein-based matrixes were quite efficient in retention of caraway oil. WPC based matrixes retained more than 80% of oil added to the emulsion. Among two milk products, SMP and WPC, the latter showed higher retention capacity for the microencapsulation. The retained amount of volatiles in SMP and WPC matrices was 76.12% and 80.71% (on the basis of the oil amount added to the emulsion) respectively.

Replacement of 10% of WPC by different maltodextrins has led to an increase of retention of volatiles from 80.71% (WPC) to 87.85% (WPC+MD N-lok). Meanwhile the SMP matrices have shown an opposite tendency: replacement of SMP by all types of carbohydrates gave an inferior retention of volatiles. The content of caraway oil retained on the surface of the capsules was not considerable and in most cases did not exceed 2.5% of the total oil.

Effectiveness of microencapsulation is the most important characteristic of the process, which can be calculated by subtracting surface oil from the amount of the total retained in the matrix oil or measured by hydrodistillation of essential oil from the matrix after washing out surface oil by an organic solvent. WPC-based matrixes (with and without MD) were the most effective matrixes in our study (Table 1). Efficiency of the systems containing WPC with each of the carbohydrates (N-lok, Encaps855, Capsul-E) was higher than that for WPC as a sole wall constituent resulting in 85.88%, 83.05%, 81.75%, and 78.81%, respectively. In general, effective characteristics of the proteins used in this study correspond to the total oil retained in the matrixes, because the major part of the oil retained was entrapped in the capsules. Among other things the retention of the core material during microencapsulation by spray drying is

Table 1 Characteristics of caraway oil encapsulation in different matrices

No	Encapsulating agent	Total oil, %	Surface oil, %	Encapsulation efficiency, %	Moisture, %
1	Whey protein concentrate (WPC)	80.71	1.9	78.81	3.50
2	WPC+MD N-lok (9:1)	87.85	1.97	85.88	2.90
3	WPC+MD Encaps 855 (9:1)	85.53	2.48	83.05	3.77
4	WPC+MD Capsul–E (9:1)	84.11	2.36	81.75	2.73
5	Skimmed milk powder (SMP)	76.12	1.98	74.14	3.34
6	SMP+ MD N-lok (9:1)	71.04	1.40	69.64	2.18
7	SMP+ MD Capsul–E (9:1)	70.86	1.02	69.84	2.50
8	SMP+ MD Encaps 855 (9:1)	69.22	1.16	68.06	3.02

affected by the properties and composition of the emulsion and by the drying conditions [12]. Considering the relatively high hydrophobicity of whey proteins, the addition of the carbohydrates enhances the hydrophilic nature of the wall system which might limit accessibility of microencapsulated oil to the diffusion process during the distillation. Young et al. also demonstrated that the yield and the efficiency of microencapsulation of anhydrous milk fat (AMF) might be enhanced by the selection of wall components exhibiting different functional properties, e.g., carbohydrates combined with whey proteins. It was demonstrated that microencapsulation efficiency of systems containing whey protein isolate (WPI) and each of the surface active carbohydrates NAT46 and ENC855 were higher (ca. 87% and 89% respectively) than those obtained for WPI or any of the NAT 46 or ENC 855 carbohydrates as a sole wall material (35%, 31%, 35%, respectively) [38].

However, in our study the addition of MD to SMP has not increased the efficiency of microencapsulation process. The efficiency values decreased from 76.12% for SMP to 71.04%, 70.86%, and 70.86% for SMP+N-lok, SMP+Capsul-E, and SMP+Encaps 855, respectively. The results suggest that in these systems associated adverse effects were introduced by the surface-active carbohydrates. The complexity of the properties of used encapsulating materials and involved process yielded rather complex results. Several theories have been developed to explain the retention of volatiles during drying of food material. Volatile losses during spray drying are associated not only with the interaction between the drying droplets and the hot air but also with the process of droplet formation-atomization [56]. Menting and Hoogstad postulated that volatile materials can leave drying droplets until the termination of the first stage of drying process, i.e., until the crust forms around the droplets [57]. Further losses can occur only if the volatiles can pass through the crust by means of diffusion in the solid or through the pores or channels. On the basis of this explanation, the type of solids, its concentration, and drying temperature are very important for their effect on crust formation. According to "selective diffusion theory" presented by Brooks [58] and Rulkens and Thijssen [59], the diffusion coefficients of water and volatiles are reduced as water concentration decreases due to drying. As a result of differences in molecular weight of water and volatiles, the reduction in the diffusivity of the volatiles is more pronounced than that of water. Once the crust has formed, volatiles diffusivity is so low that for all practical purposes the volatiles are entrapped in the drying solid matrix, while water can still diffuse through the crust. The crust therefore becomes effectively a selective membrane. Since all operating conditions of the drying process (rate and temperature) have been kept constant during the experiment, it might be that crust formation was playing a major role in obtaining different retention of encapsulated caraway oil. The WPC possessing a higher content of carbohydrates reduces the time for dry skin (crust) formation around the drying droplet (capsule), thus decreasing the losses of volatiles. Another assumption is that the superiority of WPC over the SMP material can be attributed to its relatively high lactose content. Higher amounts of lactose in WPC enhance the ratio of the capsule solidification during the drying process and essential oil droplets are locked in the dry matrix. Moreau and Rosenberg [36] have studied the microstructure of whey protein/lactose-based containing anhydrous milk fat (AMF) spray dried microcapsules. They found that partial replacement of WPI by amorphous lactose significantly limits the proportion of AMF that can be extracted from the capsules by an apolar solvent. Because it is unlikely that only molecular diffusion controls retention we assume that the loss of the volatiles in the SMP matrices might be the outcome of some other physicochemical differences between SMP and WPC.

Release of volatiles by DHS

The results of recovery of limonene and carvone from microencapsulated and pentane washed products are shown in Fig. 1. It was determined as a function of nitrogen purge time. Results reveal that compounds were released at different rates by microencapsulated products. The range of released limonene and carvone were from 0.01 μg g^{-1} for WPC+MD N-lok (9:1) to about 2.6 μg g^{-1} for SMP+MD Capsul-E (9:1) and from 0.12 μg g^{-1} for WPC+MD N-lok to 3.54 μg g^{-1} for SMP+MD Encapsul 855 (9:1), respectively. The adding of different types of MD to WPC significantly reduced the release of entrapped volatiles from capsules (from 1.15 μg g^{-1} to 0.016 μg g^{-1} and from 1.18 μg g^{-1} to 0.12 μg g^{-1} for li-

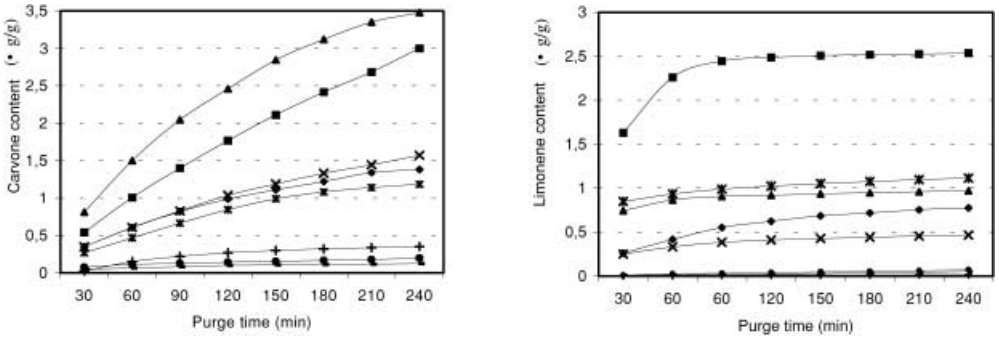

Fig. 1 Contents of limonene and carvone, released from microencapsulated caraway oil products by DHS method: -◆- SMP; -■- SMP+MD Capsul-E; -▲- SMP+MD Encaps 855; -×- SMP+MD N-lok; -✻- WPC; -●- WPC+MD Capsul-E; -+-WPC+MD Encaps 855; --- WPC+MD N-lok

monene and carvone respectively) while the addition to SMP matrix in most cases resulted in a higher amount of released volatiles. The results also support the aforementioned assumption that differences in chemical composition of matrices influence the "locking" of entrapped droplets of oil in the capsule. It can be preliminarily suggested that WPC applied together with MD can form a double layer around essential oil droplets strongly protecting the release of their constituents during the nitrogen purge. Another assumption could be that the lactose acts in its amorphous state as a hydrophilic filler or sealant that significantly limits diffusion of the volatiles through the walls of the capsule. However, investigations with model systems consisting of separate fractions of WPC would be needed to prove or reject this suggestion.

Flavor profile

The profile depends on the qualitative and quantitative composition of volatile constituents in the product. Therefore, it is important to measure the changes of these compounds during processing. Percentage concentrations of the principal constituents of caraway flavor (limonene and carvone) in pure non-encapsulated essential oil and hydrodistilled from the matrixes after spray drying are shown in Fig. 2.

In general, the ratio of limonene to carvone in the matrixes was similar to that in pure essential oil. A small decrease of limonene content in encapsulated oils has been recorded. This could be a result of volatile losses during the drying when emulsion droplets are in contact with high temperature air. Being more volatile, limonene is expected to be lost in the first place. However, a very slight increase in the percentage content of limonene can be observed in two matrices.

Evaluation of storage stability

The formation of oxidation compounds (limonene oxide isomers and *cis*-*p*-menth-2-en-ol) was measured as a function of time for determining the protective properties of capsules during storage. Monitoring was carried out under different environmental conditions, i.e., 50 °C and room temperature, in the presence and absence of light. In parallel, the samples of pure, non-encapsulated caraway oil have also been exposed for the monitoring of formation of oxidation products.

Among eight different samples SMP, SMP+N-lok, and WPC+N-lok appeared to be least resistant to oxidation (Fig. 3). As expected, oxidation products were first recorded among the samples stored at 50 °C. SMP and SMP+N-lok encapsulated caraway oil exhibited an induction period of 8 weeks during which no limonene oxide has been produced. By week 26, the value of *cis*-limonene oxide has reached the levels of 2.13 mg g^{-1} and 1.89 mg g^{-1} for SMP and SMP+N-lok samples respectively. A similar content of *trans*-limonene oxide was produced by week 26 in SMP and SMP+N-lok matrices, 2.22 mg g^{-1} and 2.34 mg g^{-1}. A WPC-based matrix with MD N-lok also contained *cis*- and *trans*-limonene oxides after 15 weeks and 13 weeks respectively. However, the amounts of limonene oxides in WPC+N-lok at the end of monitoring time was approximately four times less than in SMP and SMP+N-lok, corresponding with 0.54 mg g^{-1} and 0.45 mg g^{-1} of *cis*- and *trans*-limonene oxide. Samples stored at room temperature were more resistant to oxidation. Limonene oxides, 0.12 mg g^{-1} *cis*- and 0.18 mg g^{-1} *trans*- were recorded in SMP sample stored in light by the 20th week of storage. It seems that the oxidation processes are influenced not only by the temperature but by the light as well. The same sample of SMP stored at room temperature in the dark exhibited a three weeks longer induction period as compared to that stored in light. However, the amounts of oxides recorded by

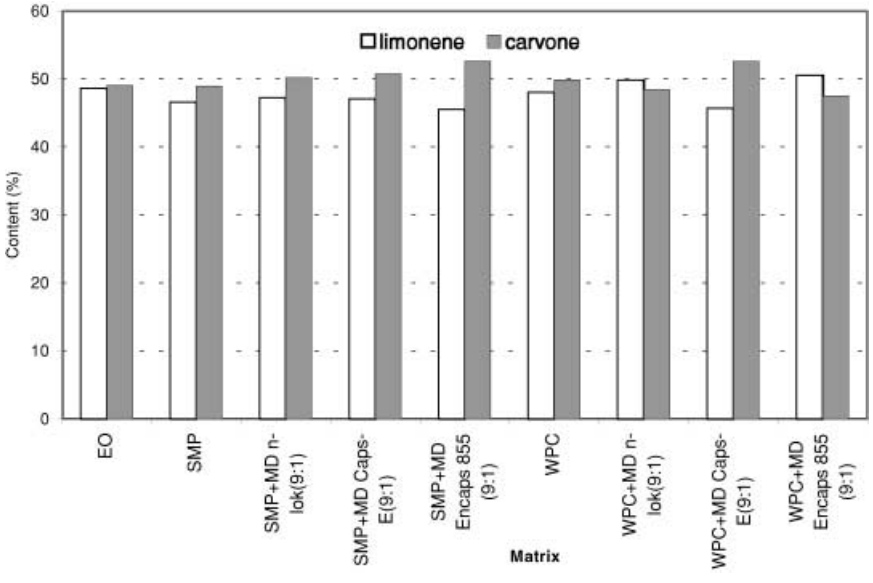

Fig. 2 Content of limonene and carvone in pure caraway essential oil (EO) compared to retention in different matrixes

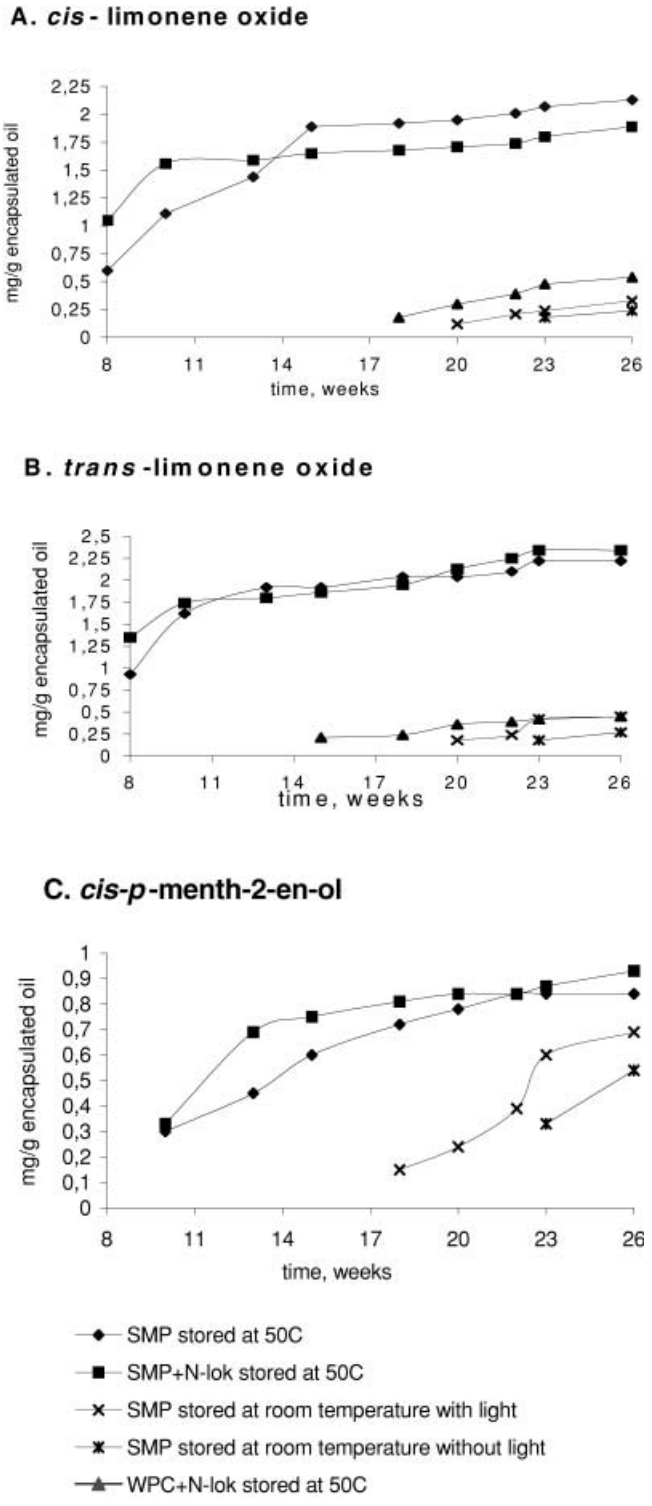

Fig. 3A–C Formation of oxidation products (*cis*- and *trans*-limonene oxides, *cis*-*p*-menth-2-en-ol) in encapsulated caraway essential oil during storage at different conditions: 50 °C, room temperature (RT) with/without light

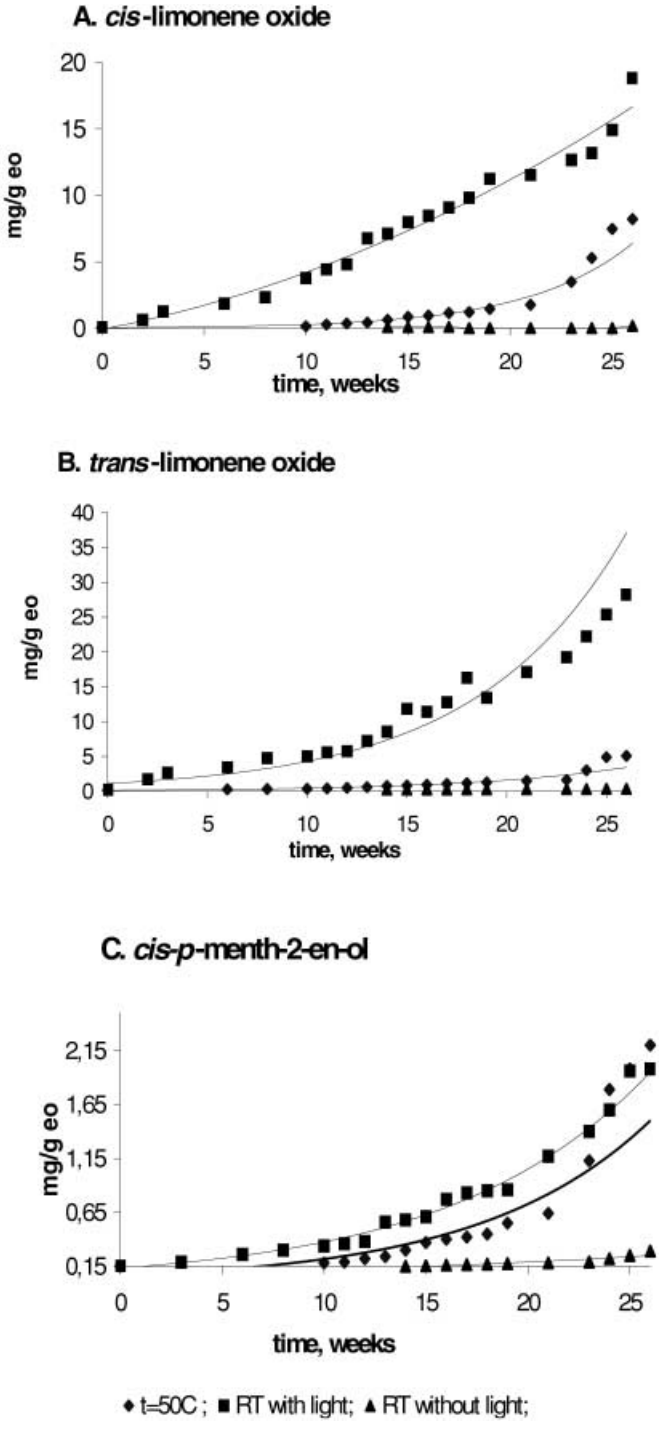

Fig. 4A–C Formation of oxidation products (*cis*- and *trans*-limonene oxides, *cis*-*p*-menth-2-en-ol) in non-encapsulated caraway essential oil during storage at different conditions: 50 °C, room temperature (RT) with/without light

week 26 were similar to those obtained at room temperature in light.

The third oxidation product was tentatively identified in our study as *cis*-*p*-menth-2-en-ol. It was found in SMP and SMP+N-lok matrices at 50 °C and in SMP samples stored at room temperature. The induction period of this component was 10 weeks for both samples of SMP and SMP+N-lok stored at 50 °C, and 18 weeks and 23 weeks for SMP sample stored in the presence and absence of light. In general, all quantities of oxidation products

formed in encapsulated oil were significantly lower compared to those in non-encapsulated oil. The finding that WPC-based microencapsulated products were consistently more stable against oxidation than SMP-based products is in agreement with the work of Kim and Morr [53] in which WPI microencapsulated orange oil was more stable against oxidation than sodium caseinate microencapsulated oil.

Nevertheless the results of storage of non-encapsulated caraway oil (Fig. 4) under the same conditions as the encapsulated one showed that the most significant influence of environment is light, followed by temperature. The sample of caraway oil stored at room temperature in the presence of daylight exhibited a three-weeks induction period for the formation of limonene oxides reaching 18.82 mg g^{-1} and 28.22 mg g^{-1} values for *cis*- and *trans*- limonene oxides respectively by the end of monitoring. Meanwhile the oxidation of non-encapsulated oil was found to be significantly slower at 50 °C: the induction period was five weeks and values of the oxides formed by the end of storage have reached 8.2 mg g^{-1} and 5.09 mg g^{-1} respectively for *cis*- and *trans*- limonene oxide. From Fig. 4 it is clear that the changes appearing in the oil stored at room temperature in the dark are not as significant as those stored in light. That tendency could not be clearly evident in the encapsulated products when oil droplets are entrapped within the capsule and protected from the light by the wall. It implies that photooxidation induced by light is more profound than by accelerated thermal degradation. This is important to bear in mind for handling and utilizing caraway essential oil.

Considering that there was no antioxidant in the encapsulated products, the storage stability was quite good for most of the products. Generally, the rate of formation of limonene oxide and other oxidation products may have been influenced by many factors such as matrix porosity to oxygen, absolute density, pro-oxidants, trace mineral, or other compounds present. The role of entrained air (i.e., air included or trapped within the particle) in determining storage stability of spray dried products has not been studied.

Release of volatiles during storage

Figures 5 and 6 represent the dynamics of the release of the aroma volatiles from encapsulated powders as a function of time. A comparison was made between powders stored at 50 °C and room temperature. As expected, lower losses of volatiles are found in the powders stored at room temperature than at 50 °C. However, qualitatively the results of aroma losses during storage follow the same tendency as in the analysis of volatile release by DHS and monitoring of storage stability; SMP based matrices exhibit higher volatile release and losses during storage time than WPC.

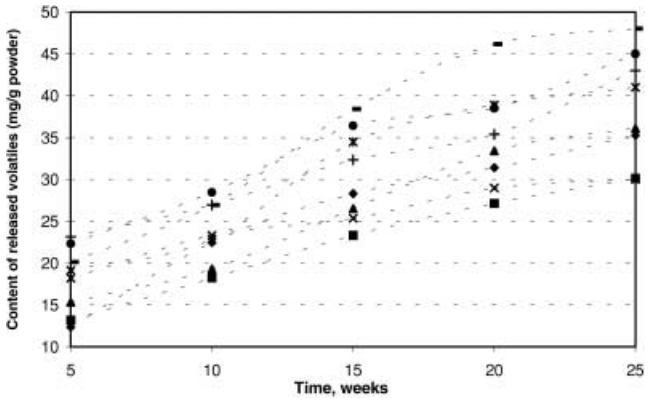

Fig. 5 Release of volatiles by different matrixes during powders storage at room temperature

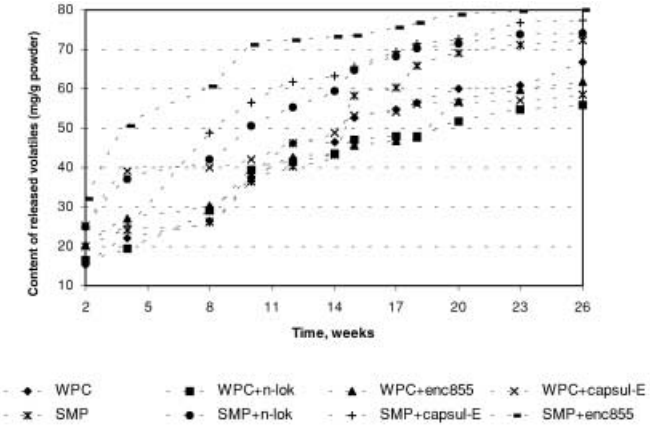

Fig. 6 Release of volatiles by different matrixes during powders storage at 50 °C temperature

Microstructure

The outer topography of spray dried microcapsules was studied by SEM and is presented in Figs. 7, 8, 9, and 10. In order to study the effect of the wall composition on the microstructure features of the spray dried microcapsules containing caraway oil, the same atomization and drying conditions were consistently maintained in this study. SEM results of spray dried WPC based matrices (Figs. 7 and 8) revealed spherically shaped particles with smooth surfaces and large variance in size. However, the surface of a few WPC capsules (Fig. 7) exhibited some holes. The matrices of WPC combined with carbohydrates (Fig. 8) have not differed greatly from sole WPC matrices; they contained less visible cracks although more dented surfaces could be observed in them compared to WPC per se. Wall composition, atomization and drying parameters, uneven shrinkage at early stages of drying were attributed to factors affecting the formation of surface indentations in spray dried particles [39, 60, 61, 62]. In 1998 Sheu and Rosenberg [49] studied how the structures of spray dried microcapsules with wall materials consisting of whey proteins and carbohydrates were affected by WPI/COH ratio and by the profile of

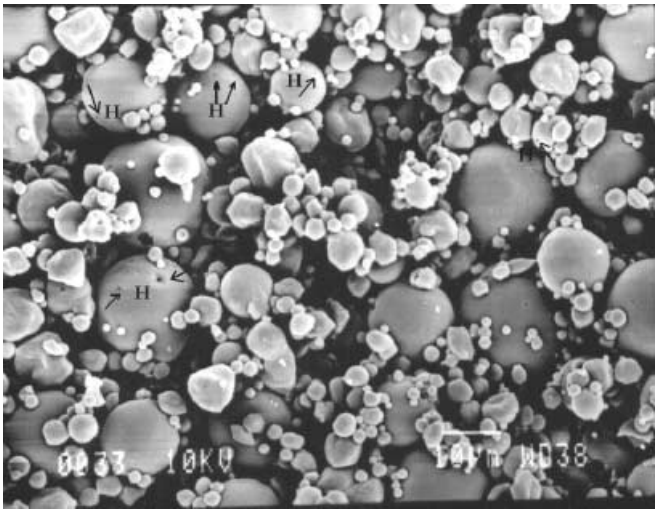

Fig. 7 Micrographs of spray dried WPC based caraway oil containing microcapsules. H=hole. *Scale bar*=10 μm

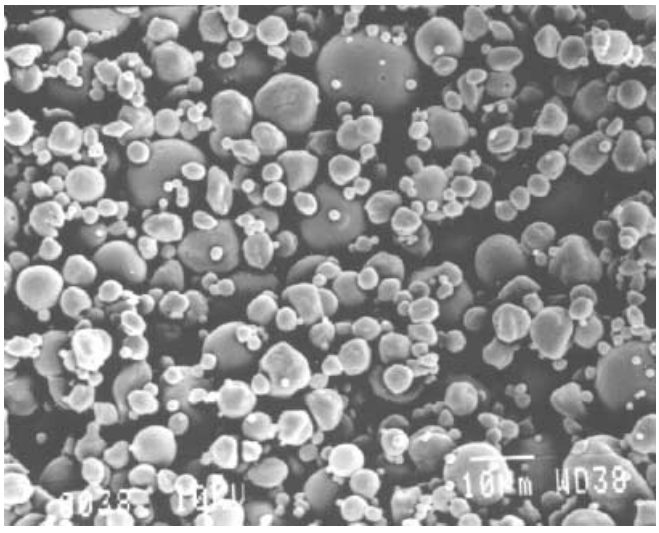

Fig. 9 Micrographs of spray dried SMP based caraway oil containing microcapsules. *Scale bar*=10 μm

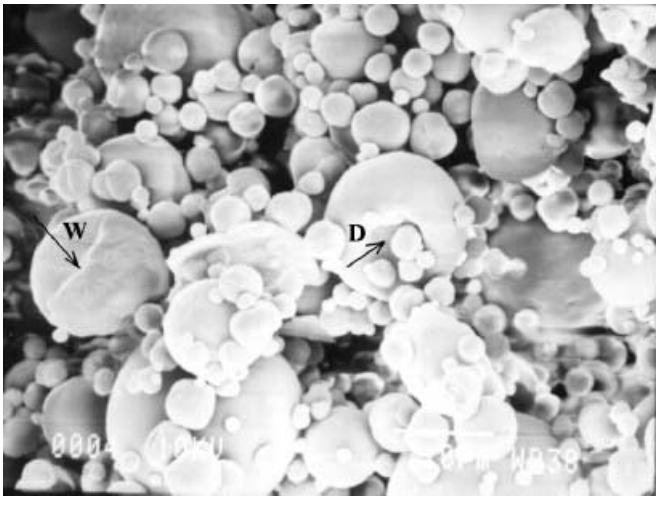

Fig. 8 Micrographs of spray dried WPC+MD Capsul-E based caraway oil containing microcapsules. W=wrinkle, D=dent. *Scale bar*=10 μm

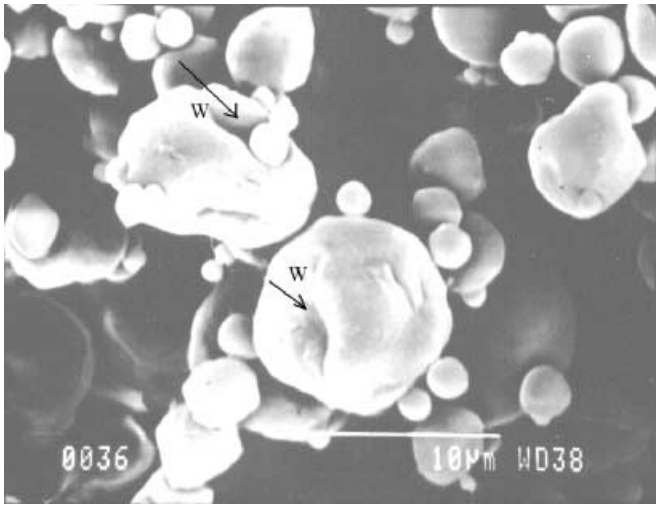

Fig. 10 Micrographs of spray dried SMP+MD Encaps 855 based caraway oil containing microcapsules. W=wrinkle. *Scale bar*= 10 μm

the carbohydrates. The results of this work suggested that the extent of surface indentation was inversely related to the content of WPI included in the wall. Another observation made in this study was dealing with the effect of the ratio of high-to-low molecular weigh (MW) solutes (included in the wall) on the structure of microcapsules; as DE value increased the proportion of capsules with caps was also increasing. The tendency to develop surface dents affected by the ratio of low-to-high molecular weight solutes contributing to the viscoelastic properties of the drying solution or emulsion was noticed by Rosenberg and Young [39]. Although the capsules were prepared from emulsions that differed in their composition by different added MDs, no significant differences in outer topography could be detected.

The surfaces of capsules with SMP-based walls were different from those made of WPC; the surface of capsules with SMP per se (Fig. 9) have less surface dents, cracks, and wrinkles compared to SMP combined with carbohydrates (Fig. 10). The presence of surface dents reported for spray dried skim milk powders has been attributed to the effect of conditions of atomization and drying on casein [60]. It was suggested that the observed surface folds pores and cracks represented the effects of mechanical stresses induced by uneven drying at different parts of the drying droplets by shrinkage of casein. It was also concluded that casein rather than lactose was probably responsible for surface dents.

Figures 11 and 12 represent the inner structure of shattered SMP and WPC capsules and show a porous

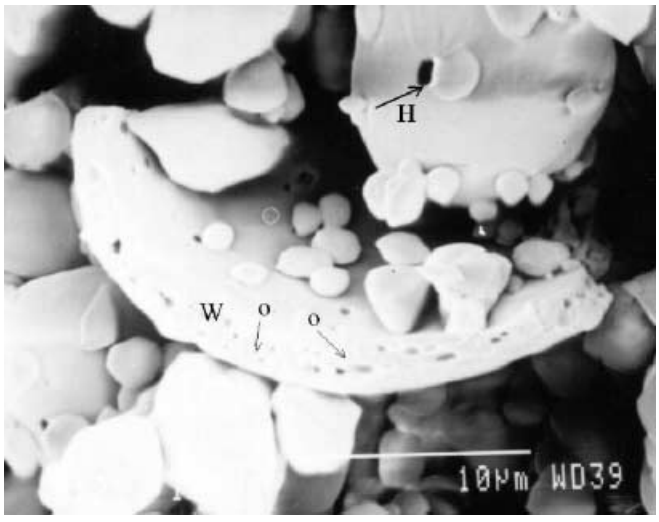

Fig. 11 Micrograph showing the inner structure of microencapsulated to WPC caraway oil matrix: W=wall of the matrix, H=hole, O=oil droplets. *Scale bar*=10 µm

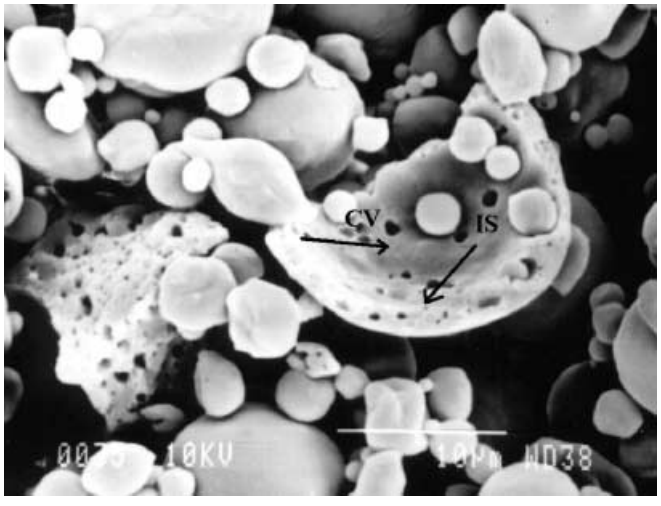

Fig. 12 Micrograph showing the inner structure of microencapsulated to SMP caraway oil matrix: CV=central void, IS=inner surface. *Scale bar*=10 µm

structure of the interior regions of the spray dried particle wall. Caraway oil (O) is organized in the form of small droplets embedded in the capsule wall (W). The existence of holes (H) on the central void (CV) surface is evident. The nature of these features is not completely clear, since there is conflicting information regarding the role of different milk constituents in affecting particle structure.

Conclusions

Milk origin products per se and in combination with carbohydrates can be successfully used as wall materials for encapsulation of caraway essential oil by spray drying. The content of the oil not entrapped by the capsules was not significant. Comparing two milk origin products, SMP and WPC, the latter exhibited better encapsulating properties.

The encapsulation efficiency can be increased by the selection of wall components that exhibit different functional properties: partial replacement of WPC by surface active carbohydrates increases retention of volatiles during spray drying and enhances protective properties of solidified capsules to oxidation and release of volatiles during the storage. The opposite tendency was observed for SMP-based matrices: the replacement of SMP by carbohydrates has resulted in the reduction of the retention of volatiles during spray drying. The latter matrices have also exhibited a lower stability to oxidation.

The percentage contents of the main flavor constituents, limonene and carvone, were only slightly different in encapsulated matrices as compared to pure oil.

The inner and outer structure features of spray dried capsules indicated that good physical protection is provided to caraway essential oil. WPC-based matrices have showed inferior structural properties to SMP.

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