AGRICULTURAL AND FOOD CHEMISTRY

Encapsulation Performance of Proteins and Traditional Materials for Spray Dried Flavors

JOSÉPHINE CHARVE* AND GARY A. REINECCIUS

Department of Food Science and Nutrition, University of Minnesota, 1334 Eckles Avenue, St. Paul, Minnesota 55108

The objective of this study was to evaluate the potential of selected proteins as alternative materials for flavor encapsulation by spray drying. Two traditional materials (gum acacia and modified starch) and three proteins (sodium caseinate, whey and soy protein isolates) were used at different infeed solid levels; test compounds included (R)-(+)-limonene and three α , β -unsaturated aldehydes ((E)-2-hexenal, (E)-cinnamaldehyde, citral). The primary criteria for performance were flavor retention during drying and protection against losses during storage. Limonene oxidation and nonenzymatic browning were investigated as two possible deterioration routes. Overall, higher infeed solids improved retention during drying and limited flavor losses (aldehydes and limonene) during storage in traditional materials only. The materials giving the highest flavor retention during drying were gum acacia (94%), modified starch (88%) and whey protein isolate (87%). Gum acacia provided the highest retention of aldehydes during storage (37 to 58%) after 28 days at 40 °C but did not afford good protection against limonene oxidation. Oppositely, protein materials effectively limited limonene oxidation (>70% retained). Nonenzymatic browning was observed for all powders prepared with proteins, especially whey protein isolate, whereas no browning occurred with traditional materials.

KEYWORDS: Encapsulation; spray drying; wall material; proteins; flavor retention; nonenzymatic browning; oxidation

INTRODUCTION

Gum acacia and modified starch have been the most common carriers used for flavor encapsulation via spray drying (1); these materials have the capacity to retain volatiles well during the drying process and protect volatiles against losses on storage. Variations in the supply of gum acacia and, recently, increasing prices of starch-based materials have led the flavor industry to seek alternative materials. Thus some flavor research has focused on the identification of new materials for spray drying; legal status, price, availability, and most of all, functionality of the material being crucial for their selection (2). Proteins, particularly milk proteins, have been suggested as alternative materials (3-6).

Proteins are widely used in the food industry but also in other fields (e.g., drug and nutrient delivery) because of their functional properties which make them of interest for flavor encapsulation. Sodium caseinate has been shown to offer good emulsifying and encapsulating properties during spray drying of lipid-containing emulsions (6, 7), however, little work has been reported on the encapsulation of flavor compounds with it. Other research has shown that whey protein may be used for the encapsulation of flavor compounds (3, 5, 8) or essential oils (9, 10). Ease of drying and subsequent flow properties of whey protein powders are proposed advantages for their use in

* Corresponding author. Tel: (1) 612-624-7717. Fax: (1) 612-625-5272. E-mail: charv002@umn.edu. spray drying operations (11). Vegetable protein, i.e. soy protein, has also been shown to provide good retention during spray drying of orange oil (4).

Although there has been extensive research on the binding of flavor compounds with proteins (for reviews see refs 12, 13), there is no mention in the literature, as far as we are aware, about the reactivity of proteins toward flavoring components during the storage of spray dried flavors. If proteins are to be used as wall materials for flavor encapsulation, we believe that this concern must be addressed. Indeed, a lot of flavor compounds contain carbonyl groups (e.g., ketones, and aldehydes) that can react with the amino groups of a protein (Schiff base formation) initiating the Maillard reaction and resulting in brown pigments as well as flavor loss.

The objective of this study was to evaluate the potential of three proteins commonly used by the food industry, sodium caseinate, whey and soy protein isolates, as alternative materials for flavor encapsulation by spray drying. Their performances were compared to traditional materials like gum acacia (mixture of polysaccharides and glycoproteins) and modified starch (polysaccharide) in terms of flavor retention during drying and protection against losses during storage.

MATERIALS AND METHODS

Materials. Citral [5392-40-5], (*E*)-2-hexenal [6728-26-3] and (*E*)cinnamaldehyde [104-55-2] were purchased from Aldrich Chemical Co. (Sigma/Aldrich, St Louis, MO) and Acros Organics (Fisher Scientific,



Figure 1. Influence of wall material choice and dryer infeed solids on volatile oil retention during spray drying. *SC 10 has a viscosity of 0.25 Pa · s when used at 10% infeed solids.

Pittsburgh, PA), respectively. Single-fold cold-pressed Valencia orange oil (90% (R)-(+)-limonene) was provided by Robertet Flavors, Inc. (Piscataway, NJ), and was used as a solvent for the chosen aroma compounds. These flavor compounds were selected for their reactivity (i.e., α,β -unsaturated aldehydes and a terpene hydrocarbon) and our desire to determine how important the Maillard reaction (aldehydes in model) and oxidation (limonene in model) are to flavor losses during the storage of flavors encapsulated by proteins. In addition, their broad use in a variety of food flavorings makes them suitable test compounds for the study. Gum acacia (GA) [Spray gum, Colloïdes Naturels International, Bridgewater, NJ], modified starch (MS) [Capsul, National Starch and Chemical Company, Bridgewater, NJ], whey protein isolate (WPI) [BiPro, Davisco Foods International Inc., Le Sueur, MN], sodium caseinate (SC) [Alanate 180, NZMP/Fonterra Proteins, Chicago Sweeteners, Des Plaines, IL] and soy protein isolate (SPI) [Pro Fam 781, ADM, Decatur, IL] were used as wall materials.

Spray Drying and Storage of Samples. Each material (ca. 2 kg) was dispersed in warm water (40 °C) at the desired solids level and kept under constant stirring overnight to ensure hydration. Carriers were prepared at equal solids levels (10%) and at equal viscosities (ca. 0.25 Pa·s) which were of the following solids levels: MS 40%, GA 35%, WPI 35%, SPI 22% and SC 10%. Prior to spray drying, aroma compounds (5% each, w/w) were blended with orange oil (85% w/w) to constitute the model flavoring. The model flavoring was then added to the carrier slurry at a 1:4 ratio flavor:carrier solids and homogenized with a benchtop, high shear mixer (Greerco Corp., Hudson, NH) at high speed for 5 min. The emulsions were spraydried in a Niro Utility Model spray dryer (Niro Atomizer Ltd., Columbia, MD). Drying conditions were maintained at inlet and exit air temperatures of 200 ± 5 °C and 100 ± 5 °C, respectively. The preparation of the nine emulsions and the spray drying operation was performed in duplicate. After cooling to room temperature, the powders were placed in open containers (thin layer) and stored in desiccators at 40 °C under controlled water activity (saturated MgCl₂ solution, $a_w = 0.33$ at 25 °C) until sampling and analysis. Two desiccators were used in total: one contained samples for flavor quantification (after drying and during storage), and one contained samples for colorimetric measurements.

Total Volatile Oil. Total volatile oil retained during drying was determined using Clevenger distillation. Approximately 20 g of spray dried powder was dissolved in 150 mL of distilled water in either a 250 or 500 mL round-bottom flask. Then, ca. 0.5 mL of silicone oil (antifoam) was added to the flask and the Clevenger trap was connected to the flask with a water-cooled condenser on top. The distillation was

carried out under constant stirring for 4 h, and the volume of distilled oil was read directly from the collection arm. The volume of oil was converted to mass by multiplying by the density of the oil (0.852 g/mL as determined gravimetrically at 25 °C). The volatile oil retention (overall aroma retention) during drying was calculated as follows:

volatile oil retention % =
$$\frac{\text{measured oil content}}{\text{theoretical oil content} \times r} \times 100$$

where the theoretical oil content was 20% assuming ideal retention, and the recovery factor r using the Clevenger apparatus was 0.88.

Retention of Individual Aroma Compounds during Spray Drying. The amounts of individual aroma compounds retained by the spray drying operation were determined by gas chromatographic (GC) analysis. Fresh powder samples were extracted using an acetoneextraction method. Approximately 0.15 g of spray dried flavor was dissolved in 0.85 g of distilled water in a screw-cap vial and mixed using a vortex mixer. Then, 4 g of an acetone solution containing 2-octanone as an internal standard (0.25 mg/g acetone) was added to the vial and mixed again. After settling, the supernatant was transferred to a 2 mL screw-cap vial and loaded into a HP 7673 automatic sampler (Hewlett-Packard, Wilmington, DE). One microliter of each extract was automatically injected in splitless mode into a HP 5890 series II GC (Hewlett-Packard, Wilmington, DE) equipped with a HP-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 μ m film thickness) (J&W Scientific, Folsom, CA) and a flame ionization detector (FID). The operating conditions were as follows: head pressure, 12 psi; helium, 1 mL/min; initial oven temperature, 50 °C increased at 10 °C/min to 140 °C with 2 min hold, then 30 °C/min to 220 °C with 2 min hold; injection port, 200 °C; FID, 250 °C. Data collection and peak area integrations were performed using the GC Chemstation software (Agilent Technologies, 2000). Citral was reported as the sum of both isomers (neral and geranial). Concentrations of individual aroma compounds (mg/g powder) in each spray dried powder were determined via regression lines ($R^2 > 0.97$) obtained from 5-point calibration curves. The aroma retentions of the individual compounds were expressed as a percentage of their initial amount in the emulsions, which were the following: 10 mg/g of solids each for citral, (E)-2-hexenal, and (E)-cinnamaldehyde, and 153 mg/g of solids for (R)-(+)-limonene.

Retention of Aroma Compounds during Storage. The amount of aroma compounds remaining in the powders was measured at different storage times. Samples were withdrawn from the stored powders on days 0, 4, 7, 14, 21 and 28, and the model flavor compounds were quantified by gas chromatography as previously described. For each compound, the remaining amount was expressed as a percentage of the initial amount after drying of the material considered.

Limonene Oxidation. The oxidative stability of limonene was expressed as the ratio of peak areas (obtained by GC) of limonene oxide isomers vs limonene as a function of storage time.

Nonenzymatic Browning. The extent of nonenzymatic browning NEB (Maillard reaction) in the stored powders was measured by monitoring the formation of brown pigments and expressed as the b^* value. Color was measured with a Minolta chromameter CR-200 (Minolta, Osaka, Japan). The instrument was calibrated on each day of analysis with a standard white plate (calibration plate CR-A43, Minolta, Osaka, Japan). Petri dishes (60×15 mm) were filled with the spray dried powders after drying and stored until analysis under conditions previously described. Color readings were taken by placing the measuring head flat against the bottom of the Petri dish to allow uniformity in the surface distribution of the sample and performed weekly for a month. The total color change Δb^* ($\Delta b^* = b^*_{28day} - b^*_{0day}$) of the powders was used to reflect the extent of browning that occurred during storage.

Statistical Analysis. All sample analyses were done in triplicate for each treatment (combination of wall material-dryer infeed solids) from each spray dried batch (2 batches). As noted earlier, encapsulation performance across carriers was based on volatile retention during drying (total oil retention and individual aroma retention), and the stability of encapsulated flavor compounds (oxidation and NEB) during storage. The effect of the wall material-dryer infeed solids on encapsulation performance was tested using a one-way analysis of variance, with batch as block, and followed by a Tukey honest

compounds ^d	Vp ^e	GA 10	GA 35	MS 10	MS 40	WPI 10	WPI 35	SPI 10	SPI 22	SC 10
(E)-2-hexenal	4.72	3.3	59.2	3.0	63.7	16.9	30.7	19.1	16.9	25.3
(R)-(+)-limonene	1.45	45.9	89.4	51.5	76.1	36.2	78.2	66.2	73.3	57.5
citral	0.09	44.8	71.3	60.6	97.7	39.3	74.8	35.1	41.7	56.1
(E)-cinnamaldehyde	0.03	24.6	55.7	48.9	85.1	46.7	62.0	35.0	35.6	43.7

^a Expressed as a percentage of the initial amounts, real amounts in the dried powders were quantified by GC-FID. ^b GA, gum acacia; MS, modified starch; WPI, whey protein isolate; SPI, soy protein isolate; SC, sodium caseinate. ^c Infeed solid levels (%) are shown in column headings along with the wall material. ^d Listed in order of elution. ^e Vapor pressures (mmHg) were calculated at 25 °C, using EPI suite (23).

significant difference test for mean separation. Statistical tests were performed using the R statistical freeware (14), and significance was declared at P < 0.05.

RESULTS AND DISCUSSION

As noted earlier our primary objective was to compare encapsulation performances of three proteins (sodium caseinate, whey and soy protein isolates) with traditional materials (gum acacia and modified starch) for flavor encapsulation by spray drying. We chose to measure performance by retention and the stability imparted to the flavoring once dry. Our choice of test compounds was based on our desire to determine how important the Maillard reaction (aldehydes in model) and oxidation (limonene in model) are to flavor loss. We recognize that there are many other performance criteria that could also have been studied such as surface oil, powder density, particle size and flowability, but these criteria were not considered to be as important to performance as those parameters selected.

An additional consideration in our experiment is the choice of dryer infeed solids. In industrial settings, materials are prepared at the highest dryer infeed solids that can readily be pumped and atomized since high dryer infeed solids strongly improves volatile retention and dryer throughput. For example, one would not choose to spray dry a material at 10% solids (the upper limit of sodium caseinate) when it might be dried at 40% infeed solids (e.g., modified starch). In this study, we used a viscosity of 0.25 Pa·s as the maximum infeed viscosity that can be efficiently atomized in our spray dryer. While we prefer to make a constant viscosity comparison since this reflects a real world situation, we have also prepared samples at constant solids for academic interest. Thus, we have chosen to evaluate the performance of each of these wall materials prepared at both equal viscosity infeeds and equal solids infeeds.

Volatile Oil Retention during Drying. The influences of infeed solids content and type of wall material on volatile oil retention during spray drying are presented in **Figure 1**. As expected, the retention of volatiles improved when wall materials were prepared at higher infeed solid levels. This is evident by comparing the left side of the figure to the corresponding sample on the right side (except for sodium caseinate since it could not be dried at higher infeed solids). The materials giving the highest flavor retention were gum acacia (94%), modified starch (88%) and whey protein isolate (87%). These materials have fairly low viscosity in solution and thus can be used at high infeed solids levels (35–40% solids).

The impact of dryer infeed solids levels on volatile retention has been known for many years (15-17). It is generally agreed that higher solid levels provide reduced mobility of the aroma compounds in the wall material and have shorter times to form a protective shell around them. These factors lead to better flavor retention (17, 18). The type of wall material is also known to affect the retention of volatiles (8, 15) as shown by the data obtained when all materials were prepared at 10% infeed solids levels (**Figure 1**). SPI, MS and SC were more effective than GA and WPI at 10% solids, which agree with the findings of Kim and Morr (4), who compared the performance of various proteins with gum acacia. Observed differences in volatile retention may be explained by different film forming or emulsification abilities of the materials, although all materials used are known for their good film forming and emulsification properties (19). We did not make any measurements of either carrier property.

Of the proteins considered, whey protein isolate retained flavorings as well as the traditional flavor carriers. This result is supported by previous studies which have shown good retention of volatiles with WPI (11, 17, 20). Good retention during drying can be explained by the good emulsification and binding properties of β -lactoglobulin, the major whey protein (21, 22).

Retention of Individual Aroma Compounds during Spray Drying. Comparisons based only on overall retention (measured by volatile oil content) are not entirely satisfactory to make final conclusions about the encapsulation performance of a given material. The retention of individual aroma compounds after spray drying is also of importance as it may change the final flavor profile. As seen from **Table 1**, the flavor profile in the dry powders differs across carrier materials. This results in one of the most problematic issues in producing spray dried flavorings: that of producing a dry flavoring with the same sensory characteristics as the initial liquid flavoring. Thus, we are concerned not only with the total or overall flavor retention but also with the retention across volatiles being spray dried.

Overall, (*E*)-2-hexenal was very poorly retained during drying compared to other volatile compounds. (*R*)-(+)-limonene was very well retained among materials followed by citral, whereas (*E*)-cinnamaldehyde had varying retention levels across the materials (i.e., compound having the highest retention in WPI 10 and the lowest in GA 35). High losses of (*E*)-2-hexenal are primarily due to its relatively small molecular size and high vapor pressure (4.72 mmHg) compared to the other model compounds used in this study. This is consistent with other research (8, 15). It would appear inconsistent that (*E*)-cinnamaldehyde has the lowest vapor pressure (as a pure compound) but not the best retention; although one has to recall that vapor pressure *in the infeed system* and molecular weight of the compound are major factors governing retention during drying.

Finally, infeed solids also had a major influence on individual volatile retention during drying. For (E)-2-hexenal (most volatile), retention increased about 20-fold when higher solids were used with GA and MS. This is consistent with other published works, for example, Reineccius et al. (16) who reported a large improvement in the retention of highly volatile compounds when higher solids were used (rapid membrane formation).

Retention of Aroma Compounds during Storage. The overall stability (i.e., ability to maintain initial flavor levels) of the dried flavors during storage was assessed by measuring the



Figure 2. Retention during storage of (E)-2-hexenal, citral, (E)-cinnamaldehyde and (R)-(+)-limonene spray dried with different wall materials at infeed solids of equal viscosity.



Figure 3. Influence of infeed solids on the retention during storage of (E)-2-hexenal spray dried in proteins and traditional materials.

amounts of aroma compounds remaining in the powders over time. Any decrease in flavor levels reflected the overall loss (sum of all loss mechanisms, because of either their reactivity with other compounds or their evaporation) of volatiles in the powders. Figure 2 illustrates the data trends seen at the highest solids content for each material. At both high and low infeed solids, three loss profiles were identified among the compounds studied: (1) fast and severe loss ((E)-2-hexenal, citral), (2) constant rate and high loss ((E)-cinnamaldehyde), and (3) moderate loss ((R)-(+)-limonene). Overall, (E)-2-hexenal was lost to the greatest extent during storage, being almost entirely depleted by the end of the storage in a majority of the spray dried powders. Its initial loss was faster than that of the other aldehydes with less than 20% of the initial flavor level remaining after only two weeks of storage, except when encapsulated in GA 35 (52% remaining). Severe losses of citral also occurred although its depletion was slower than that of (E)-2-hexenal. (E)-Cinnamaldehyde losses were nearly linear with time, as opposed to (E)-2-hexenal and citral. By the end of the storage, (E)-cinnamaldehyde levels ranged between 12 and 77% with the highest retention for GA 35, and the lowest for MS 10 and GA 10. Finally, (R)-(+)-limonene underwent the least losses with up to 86% retained when encapsulated in proteins (i.e., SPI 22 and WPI 35).

Infeed solids appeared to have a major influence on volatile retention during storage for traditional materials only. **Figure 3** includes data for (E)-2-hexenal only as data for other model compounds were similar in overall trend. Better retention over time was achieved when either gum acacia or modified starch was prepared at their highest solids content. This may have been due to changes in particle structure (e.g., less void volume, or surface cracks) when spray dried at higher infeed solids.

Lastly, gum acacia (35% solids) clearly provided the best retention of the aldehydes during storage while MS 40, WPI

35 and SPI 22 performed poorly; even though they had shown good retention during drying. This is a good illustration of why encapsulation performances of a given material should always be assessed for retention both during drying and storage. On the other hand, protein materials gave better protection to (R)-(+)-limonene than the traditional flavor carriers.

Our study was designed to evaluate the overall flavor losses during storage of the different materials and cannot differentiate between evaporative and chemical losses of the volatiles. However, limonene oxidation and nonenzymatic browning were investigated as two possible deterioration routes.

Limonene Oxidation. (R)-(+)-Limonene losses were primarily due to oxidation as oxidation products (i.e., limonene oxide isomers) were formed (Figure 4). Protein materials gave better protection to (R)-(+)-limonene than the traditional flavor carriers by limiting its oxidation (up to 80-times difference in oxidation between samples). This result concurs with previous works which showed that proteins (i.e., whey) effectively limit the oxidation of the core material (e.g., orange oil (4), milk fat (24, 25), fish oil (26), and conjugated linoleic acid (27)). Protein-based particles were proposed to be less permeable to oxygen than the traditional flavor carriers and were free of cracks. Both factors would afford protection to the core material (4, 28-30). One also notes that limonene oxidation was higher when materials were spray dried at lower infeed solids levels (10%), especially for gum acacia and modified starch. This observation is consistent with the earlier observation that volatile retention during storage was consistently improved when a material was spray dried at higher infeed solids (Figure 3).

Nonenzymatic Browning. Nonenzymatic browning has been extensively studied in food systems as it influences the final quality of a product in terms of color, nutritional quality and flavor. When considering volatile encapsulation by protein



Figure 4. Limonene oxidation during storage of spray dried powders with different wall materials and infeed solids contents.

materials, especially carbonyls, it is essential to determine if the system will be stable during storage. If NEB were occurring, the color of the dried powders would be affected (i.e., browning) and changes in the flavor profile would occur. Consequently, we evaluated the extent of NEB in the spray dried powders by monitoring browning ($\Delta b^* > 0$) during storage. Results are reported in **Figure 5**.

Powders prepared with whey protein isolate for wall material underwent major changes in color (Δb^*) during storage, followed by sodium caseinate and then soy protein isolate. Most of the brown pigments were formed during the first week of storage, and then formation tended to level off. On the other hand, powders prepared with modified starch and gum acacia did not brown. Finally, there were no significant differences in Δb^* for a given material spray dried at different infeed solids levels.

Numerous studies have reported on the reaction of aroma compounds with proteins in solutions or model systems; however, to our knowledge, there is limited literature on the stability during storage of aroma compounds spray dried with proteins. Bangs and Reineccius (31) mentioned the reactivity of proteins with carbonyls as a limiting factor for their use in production of dried flavors; it was also mentioned by Brueckner et al. (11), but they did not investigate it further. Interestingly, chemical reactions between the wall material and volatiles during storage of dried flavors were shown to be responsible for 80% of the total aroma losses in dried flavorings encapsulated with whey protein (32) but no relationship between NEB and volatile losses was established.

Relating observed color changes to the disappearance of aroma compounds in the dried protein powders, we believe that the rapid formation of brown pigments resulted principally from the reaction of (E)-2-hexenal with the free amino groups of proteins (Schiff base formation initiated NEB). Earlier research reported the binding of aldehydes and particularly 2-alkenals with proteins. Partial reversible binding was observed with soy and whey proteins (33-35), and recently, covalent binding of (E)-2-hexenal with lysyl and histidyl residues of whey protein and sodium caseinate, along with browning of the media, was



Figure 5. Color differences Δb^* after storage of flavors spray dried with different wall materials and infeed solids contents.

observed (36). Further research is needed to understand the mechanisms and kinetics involved in NEB of stored spray dried flavors.

Few studies have established a relationship between amino acid losses and reactions with aldehydes associated with flavorings (e.g., refs 36, 37). In the present study, we observed that differences in visible browning among the protein carriers were consistent with the lysine content: whey protein isolate (9.6 g of lysine/100 g of protein), sodium caseinate (8.2 g of lysine/100 g of protein), soy protein isolate (6.4 g of lysine/ 100 g of protein), gum acacia (0.06 g of lysine/100 g of gum) (38-40). The absence of browning in powders from traditional carriers was expected as there are no, or few, amino acids present in starch and gum acacia (2.03% proteinaceous content), respectively (40). While we are commenting on the observed color formation during storage and linking it with aldehyde:amino acid reactions, we acknowledge that aldehydes may be lost due to oxidation into their respective acids or evaporation.

In summary, this study evaluated the potential of selected proteins for spray drying of flavors at different solids contents. Flavor retention during drying and protection against losses during storage were examined. Infeed solids levels had a strong impact on spray dried powder performance during drying and subsequent storage. Higher infeed solids improved retention while drying and limited flavor losses (aldehydes and limonene) due to storage in traditional materials only.

Limonene oxidation was more pronounced in gum acacia and modified starch, whereas proteins effectively reduced its oxidation. However, nonenzymatic browning occurred in powders prepared with proteins due to the reaction between aldehydes and the amino groups of proteins. Of the proteins considered, sodium caseinate was the least effective carrier material overall (i.e., poor flavor retention and substantial NEB during storage). This carrier performed poorly due to the low level of infeed solids possible (limited by viscosity) and its susceptibility to browning (i.e., lysine content). On the other hand, whey and soy protein isolates were good materials for the production of dried flavors based on volatile retention during drying. However, they performed poorly during storage as nonenzymatic browning occurred. The

Encapsulation Materials for Dried Flavors

choice of using proteins for flavor encapsulation depends on the aroma system being encapsulated. If the flavoring does not contain any carbonyl compounds, it could quite effectively be encapsulated in a protein matrix.

Further research is needed to examine the reactivity of proteins with other chemical groups (e.g., saturated aldehydes, ketones, esters) during the storage of spray dried powders. Additionally, the sensory impact of using proteins as wall material needs to be examined since the release properties of the dried flavors in a final product can be modified through chemical interactions.

ABBREVIATIONS USED

GA, gum acacia; MS, modified starch; WPI, whey protein isolate; SC, sodium caseinate; SPI, soy protein isolate; GC, gas chromatography; FID, flame ionization detector; NEB, nonenzymatic browning.

LITERATURE CITED

- Gharsallaoui, A.; Roudaut, G.; Chambin, O.; Voilley, A.; Saurel, R. Applications of spray-drying in microencapsulation of food ingredients: An overview. *Food Res. Int.* 2007, 40, 1107–1121.
- (2) Reineccius, G. A. Spray drying. In *Flavor Chemistry and Technology*, 2nd ed.; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2006; pp 367–375.
- (3) Sheu, T.; Rosenberg, M. Microencapsulation by spray drying ethyl caprylate in whey protein and carbohydrate wall systems. <u>J. Food</u> <u>Sci.</u> 1995, 60, 98–103.
- (4) Kim, Y. D.; Morr, C. V. Microencapsulation properties of gum arabic and several food proteins: Spray-dried orange oil emulsion particles. *J. Agric. Food Chem.* **1996**, *44*, 1314–1320.
- (5) Rosenberg, M.; Sheu, T. Microencapsulation of volatiles by spraydrying in whey protein-based wall systems. *Int. Dairv J.* 1996, 6, 273–284.
- (6) Hogan, S. A.; McNamee, B. F.; O'Riordan, E. D.; O'Sullivan, M. Microencapsulating properties of sodium caseinate. <u>J. Agric.</u> Food Chem. 2001, 49, 1934–1938.
- (7) Vega, C.; Roos, Y. H. Spray-dried dairy and dairy-like emulsions-Compositional considerations. <u>J. Dairy Sci.</u> 2006, 89, 383–401.
- (8) Bangs, W. E.; Reineccius, G. A. Influence of dryer infeed matrices on the retention of volatile flavor compounds during spray drying. *J. Food Sci.* **1981**, *47*, 254–259.
- (9) Bylaite, E.; Venskutonis, P. R.; Mapdpieriene, R. Properties of caraway (*Carum carvi L.*) essential oil encapsulated into milk proteinbased matrices. *Eur. Food Res. Technol.* 2001, 212, 661–670.
- (10) Baranauskiene, R.; Venskutonis, P. R.; Dewettinck, K.; Verhe, R. Properties of oregano (*Origanum vulgare L.*), citronella (*Cymbopogon nardus G.*) and marjoram (*Majorana hortensis L.*) flavors encapsulated into milk protein-based matrices. <u>Food Res.</u> <u>Int</u> 2006, 39, 413–425.
- (11) Brueckner, M.; Bade, M.; Kunz, B. Investigations into the stabilization of a volatile aroma compound using a combined emulsification and spray drying process. *Eur. Food Res. Technol.* 2007, 226, 137–146.
- (12) Guichard, E. Interactions between flavor compounds and food ingredients and their influence on flavor perception. *Food Rev. Int.* 2002, *18*, 49–70.
- (13) Tromelin, A.; Andriot, I.; Guichard, E. Protein-flavour interactions. In *Flavour in Food*; Voilley, A., Etiévant, P., Eds.; Woodhead Publishing Ltd.: Cambridge, U.K., 2006; pp. 172–207.
- (14) R Development Core Team. R: A language and environment for statistical computing. 2007, v. 2.5.1., http://www.r-project.org/.
- (15) Leahy, M. M.; Anandaraman, S.; Bangs, W. E.; Reineccius, G. A. Spray drying of food flavors. II. A comparison of encapsulating agents for the drying of artificial flavors. *Perfum. Flavor.* 1983, 8, 49–52,55–56.
- (16) Reineccius, G. A.; Bangs, W. E. Spray-drying of food flavours. III. Optimum infeed concentrations for the retention of artificial flavors. *Perfum. Flavor.* **1985**, *9*, 27–29.

- (17) Rosenberg, M.; Kopelman, I. J.; Talmon, Y. Factors affecting retention in spray-drying microencapsulation of volatile materials. *J. Agric. Food Chem.* **1990**, *38*, 1288–1294.
- (18) Reineccius, G. A.; Anandaraman, S.; Bangs, W. E. Spray-drying of food flavors. I. Theory of flavor retention. *Perfum. Flavor.* **1982**, 7, 1–6.
- (19) Madene, A.; Jacquot, M.; Scher, J.; Desobry, S. Flavour encapsulation and controlled release - A review. *Int. J. Food Sci. Tech.* 2006, 41, 1–21.
- (20) Reineccius, G. A.; Liardon, R.; Luo, Z. The retention of aroma compounds in spray dried matrices during encapsulation and storage. In *Flavour Research at the Dawn of the Twenty-First Century, Proceedings of the 10 th Weurman Flavor Research Symposium, Beaune, France, June 25–28, 2002*; LeQuéré, J. L., Etiévant, P. X., Eds.; Lavoisier: Cachan, France, 2003; pp 3–8.
- (21) Pelletier, E.; Sostmann, K.; Guichard, E. Measurement of interactions between β-lactoglobulin and flavor compounds (esters, acids, and pyrazines) by affinity and exclusion size chromatography. <u>J.</u> <u>Agric. Food Chem.</u> **1998**, *46*, 1506–1509.
- (22) Guichard, E.; Langourieux, S. Interactions between β-lactoglobulin and flavour compounds. *Food Chem.* 2000, *71*, 301–308.
- (23) U.S. Environmental Protection Agency. EPI Suite. 2007, Estimation Programs Interface Suite for Microsoft Windows v3.20., http://www.epa.gov/oppt/exposure/pubs/episuite.htm.
- (24) Young, S. L.; Sarda, X.; Rosenberg, M. Microencapsulating properties of whey proteins. 1. Microencapsulation of anhydrous milk fat. <u>J. Dairy Sci</u>. **1993**, *76*, 2868–2877.
- (25) Moreau, D. L.; Rosenberg, M. Oxidative stability of anhydrous milkfat microencapsulated in whey proteins. <u>J. Food Sci.</u> 1996, 61, 39–43.
- (26) Kagami, Y.; Sugimura, S.; Fujishima, N.; Matsuda, K.; Kometani, T.; Matsumura, Y. Oxidative stability, structure, and physical characteristics of microcapsules formed by spray drying of fish oil with protein and dextrin wall materials. <u>J. Food Sci</u>. 2003, 68, 2248– 2255.
- (27) Jimenez, M.; Garcia, H. S.; Beristain, C. I. Spray-dried encapsulation of conjugated linoleic acid (CLA) with polymeric matrices. *J. Sci. Food Agric*. 2006, *86*, 2431–2437.
- (28) Westing, L. L.; Reineccius, G. A.; Caporaso, F. Shelf life of orange oil: effects of encapsulation by spray-drying, extrusion, and molecular inclusion. In *Flavor Encapsulation*; Risch, S. J., Reineccius, G. A., Eds.; ACS Symposium 370; American Chemical Society: Washington, DC, 1988; pp 110–121.
- (29) Baisier, W.; Reineccius, G. A. Spray drying of food flavors. V. Factors influencing shelf-life of encapsulated orange peel oil. *Perfum. Flavor.* **1989**, *14*, 48, 50, 52, 53.
- (30) Bertolini, A. C.; Siani, A. C.; Grosso, C. R. F. Stability of monoterpenes encapsulated in gum arabic by spray-drying. <u>J.</u> <u>Agric. Food Chem.</u> 2001, 49, 780–785.
- (31) Bangs, W. E.; Reineccius, G. A. Corn starch derivatives. Possible wall materials for spray-dried flavor manufacture. In *Flavor Encapsulation*; ACS Symposium Series 370; Risch, S. J., Reineccius, G. A., Eds.; American Chemical Society: Washington, DC, 1988; pp 12–28.
- (32) Dronen, D. M.; Reineccius, G. A. Volatile loss from dry food polymer systems resulting from chemical reactions. In *Flavour Science. Recent Advances and Trends*, Developments in Food <u>Science ed.</u>; Bredie, W. L. P., Petersen, M. A., Eds.; Elsevier: Amsterdam, The Netherlands, 2006; Vol. 43, pp 469–472.
- (33) Gremli, H. A. Interaction of flavor compounds with soy protein. J. Am. Oil Chem. Soc. 1974, 51, 95A–97A.
- (34) Mills, O. E.; Solms, J. Interaction of selected flavour compounds with whey proteins. <u>Lebensm.-Wiss. -Technol</u>. 1984, 17, 331–335.
- (35) Zhou, Q.; Cadwallader, K. R. Effect of flavor compound chemical structure and environmental relative humidity on the binding of volatile flavor compounds to dehydrated soy protein isolates. *J. Agric. Food Chem.* 2006, *54*, 1838–1843.
- (36) Meynier, A.; Rampon, V.; Dalgalarrondo, M.; Genot, C. Hexanal and t-2-hexenal form covalent bonds with whey proteins and sodium caseinate in aqueous solution. *Int. Dairy J.* 2004, *14*, 681–690.

- (37) Schirlé-Keller, J. P. Flavor interactions with fat replacers and aspartame. Ph.D. dissertation, University of Minnesota, Saint Paul, MN, 1995; pp 111–138.
- (38) Belitz, H.-D.; Grosch, W.; Schieberle, P. Milk and dairy products. In *Food Chemistry*, 3rd revised ed.; Belitz, H.-D., Grosch, W., Schieberle, P., Eds.; Springer: Berlin, Germany, 2004; p 509.
- (39) Belitz, H.-D.; Grosch, W.; Schieberle, P. Legumes. In *Food Chemistry*, 3rd revised ed.; Belitz, H.-D., Grosch, W., Schieberle, P., Eds.; Springer: Berlin, Germany, 2004; p 749.
- (40) Randall, R. C.; Phillips, G. O.; Williams, P. A. Fractionation and characterization of gum from *Acacia senegal*. <u>Food Hydrocolloids</u> 1989, 3 (1), 65–75.

Received for review October 30, 2008. Revised manuscript received January 21, 2009. Accepted January 24, 2009.

JF803365T