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Retention of a European Pear Aroma Model Mixture Using Different Types of Saccharides

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Eight types of microcapsules of European pear (La France) aroma model mixture were prepared, and their retained aroma components and sample microstructures (both surface and cross-section) were compared. The La France pear aroma model mixture was prepared by the mixing of hexanal and five kinds of esters. α-Cyclodextrin (α-CD), gum arabic (GA), soybean soluble polysaccharide (SSPS), and highly branched cyclic dextrin (HBCD) were used as carrier solids, and spray drying and freeze drying comprised the drying methods. The mean particle size of the microcapsules ranged from 8.34 μm for the microcapsules with α-CD to 9.67 μm for those with SSPS. The total aroma contents were different depending upon the microencapsulation systems (1.35 g/100 g of microcapsules for the spray-dried microcapsules with HBCD to 14.1 g/100 g of microcapsules for the freeze-dried microcapsules with GA). The microcapsules with α-CD and GA were stable against heat treatment (40, 80, or 120 °C for 60 min) under nitrogen gas flow.

KEYWORDS: Microcapsule; cyclodextrin; flavor; aroma; pear; La France

INTRODUCTION

Microencapsulation of liquid flavor compounds is an important technique in the food industry, because it provides easy handling, improves the chemical stability of flavor compounds, and permits the controlled release of flavor compounds. Many investigations have focused on preparing various microencapsulated flavors [limonene (*1*−*4*), menthol (*5*, *6*), vanillin (*7*), lemon oil (*8*, *9*), orange peel oil (*10*−*12*), shiitake (*Lenthinus Edodes*) flavor (*13*, *14*), essential oils of thyme, oregano, and cassia (*15*), durian flavor (*16*), and cheese aroma (*17*)].

A number of mechanisms for the flavor retention in microencapsulated products have been discussed. For example, in the microencapsulated flavors prepared using CDs (cyclodextrins), the flavor molecules were usually included in the CD cavity (*18*−*24*). Matsui et al. (*25*) have noted that β-CD and ethyl hexanoate, the key flavor components of pineapple and strawberry, form inclusion complexes. In our previous paper (*26*), we analyzed the ^{1}H NMR spectra of the α-CD−butyl acetate complex and α-CD−hexyl acetate complex and clarified the CD−ester inclusion structures. In contrast to these preparations, some microencapsulated flavors prepared by spray drying retain flavor components in the wall matrix of microcapsules as small droplets (*27*, *28*). Kim and Morr (*27*) have used soy protein to prepare microcapsules of orange oil and have discovered the presence of small orange oil droplets in the wall matrix by means of confocal scanning laser microscopy observations. Soottitantawat et al. (*28*) have employed a blend of gum arabic (GA) and maltodextrins to prepare microcapsules of D-limonene, ethyl butyrate, or ethyl propionate; their SEM (scanning electron microscopy) observations of the cross-section of the microcapsules have also revealed the presence of small droplets in the wall matrix. Other mechanisms for flavor retention have also been suggested (e.g., sorption of flavor on constituents) (*29*).

As mentioned above, the flavor components are retained in the microcapsules by various manners according to the microencapsulation systems. Because microcapsules retain flavor components in different ways depending upon the system used, our goal in this study was to clarify the particular properties of microcapsules prepared by various microencapsulation systems. To this end, we prepared eight types of microcapsules of the European pear (La France) aroma model mixture (using four types of carrier solids and two types of drying methods) and compared the amount of retained aroma components and their microstructures (both surface and cross-section). In addition, we investigated the multiple effects produced by the mixing of two carrier solids (α-CD and GA) for aroma components retention and the stability of microcapsules against heat treatment. Because the saccharides are popular microencapsulation carrier solids, we chose four different types of saccharides for this role [α-CD, GA, soybean soluble polysaccharide (SSPS), and highly branched cyclic dextrin (HBCD)]. Of the various CDs (α-, β-, or γ-CD), we employed α-CD as the carrier solid, because it is most effective for the retention of the La France pear aroma components (*26*).

MATERIALS AND METHODS

Test Materials. α-CD (purity >98%) was purchased from Bio Research Corp. of Yokohama, Ltd., and GA from Wako Pure Chemical Industries, Ltd. SSPS (trade name SOYAFIBE-S EN100) was supplied by Fuji Oil Chemical Co., Ltd. HBCD (*30*, *31*) (trade name Cluster Dextrin) was supplied by Ezaki Glico Co., Ltd. Before use, α-CD, GA, SSPS, and HBCD were dried for 7 days at 6.7 kPa and 70 °C using a temperature-controlled vacuum drier (model DP-61, Yamato Scientific, Ltd.). The extra-pure grade esters and aldehyde used for the La France

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Table 1. Composition of La France Pear Aroma Model Mixture

compound	% (w/w)
hexanal	1.16
propyl acetate	6.41
butyl acetate	44.21
3-methylbuthyl acetate	0.17
pentyl acetate	1.30
hexyl acetate	46.75
total	100.00

Table 2. Particle Sizes and Water Contents of Spray Dried Microcapsules

	particle size[a] (μm)	water content % (w/w)		particle size[a] (μm)	water content % (w/w)
α-CD	8.34	4.47	SSPS	9.67	4.34
GA	8.43	4.73	HBCD	9.05	5.35

[a] Median diameter. α-CD, α-cyclodextrin; GA, gum arabic; SSPS, soybean soluble polysaccharide; and HBCD, highly branched cyclic dextrin.

pear aroma model mixture and the other organic chemicals needed for the analysis were obtained from Kanto Kagaku, Ltd.

Preparation of La France Pear Aroma Model Mixture and the Sensory Test. A mixture of hexanal with five kinds of esters was used as the La France pear aroma model mixture. Its composition is shown in **Table 1**. Thirty milligrams of the model mixture was added to 1 L of distilled water and agitated vigorously using a homogenizer (model GLH-115, Yamato Scientific, Ltd.). The solution was used as the sample for the sensory test. The pulp of La France pear, grown in Yamagata Pref. in 2005, was homogenized with a homogenizer (model AM-10, Nihonseiki Kaisha, Ltd.) and centrifuged (4220*g*, 4 °C, 20 min). The supernatant produced was used as the La France pear juice for the sensory test. The La France pear juice and the model mixture aqueous solution (30 mL each) were presented to 22 panelists in glass vials (33 mm i.d. × 70 mm high) with a cap. For the sensory evaluation, the cap was removed and the samples were sniffed by the panelists (at room temperature, ca. 20 °C), who consisted of 17 male and 5 female staff of the Yamagata Research Institute of Technology. They were asked to assess the degree of similarity between the model mixture aqueous solution and the La France pear juice as one of the following three scores: 1, extremely similar to La France pear aroma; 2, moderately similar to La France pear aroma; and 3, different from La France pear aroma.

Preparation of Microencapsulated Model Mixtures. In the first step in the preparation of the microencapsulated model mixtures, 30 g of α-CD, GA, SSPS, or HBCD was dissolved in 120 mL of distilled water. After the addition of 15 g of the model mixture, the solution was homogenized at 10000 rpm for 5 min (model GLH-115, Yamato Scientific, Ltd.) and then freeze dried (model FD-5N, Tokyorikakikai Co.) or spray dried (model GA32, Yamato Scientific, Ltd.). The homogenized samples for freeze drying were placed in a stainless steel vessel (ca. 120 mm wide × 100 mm in depth × 50 mm high), frozen at −80 °C in a freezer, and freeze-dried (pressure, 20 Pa; final temperature, 25 °C). After they were freeze dried, the samples (bulk microencapsulated model mixture) were ground into powder at 5000 rpm for 2 min with a homogenizer (model AM-10, Nihonseiki Kaisha, Ltd.). The operating conditions for spray drying were as follows: inlet temperature, 150 °C; outlet temperature, 96 °C; atomizing air pressure, 0.1 MPa; and drying air flow, 0.44 m^3/min. All of the microcapsules were stored at −80 °C in a freezer until used.

Analysis of Aroma Components Retained in Microencapsulated Model Mixture. The aroma components retained in the microencapsulated model mixtures were determined according to the method of Soottitantawat et al. (*28*, *32*), except that the 0.3 g sample of the microcapsule was dissolved in 6 mL of distilled water in a glass screw-top test tube. Then, 2 mL of hexane was added to the solution and mixed vigorously using a vortex mixer for 1 min at room temperature. The mixture was next heated at 90 °C for 30 min with intermittent shaking and centrifuged at 1200*g* at room temperature for 30 min; finally, the hexane layer was decanted. The aroma components extracted in the hexane layer were analyzed by a gas chromatograph (model GC-17A, Shimadzu Corp., Ltd.), using methyl butyrate as an internal standard. The samples were analyzed three times, and the data were presented as an average value. The operating conditions for the gas chromatography analysis were as follows: column, DB-WAX (0.53 mm i.d. × 30 m long, 1.0 μm film thickness, J&W Scientific, Ltd.); carrier gas, He at 22 kPa; column temperature, 40 °C (5 min) and 40 → 130 °C (3 °C/min); and detector, flame ionization detector operated at 250 °C.

Evaluation of the Stability of Spray-Dried Microencapsulated Model Mixtures against Heat Treatment. The spray-dried microencapsulated model mixtures with GA or α-CD (1.0 g) were placed in a glass tube (12 mm i.d. × 70 mm long). Nitrogen gas was passed through the glass tube (20 mL/min), and the tube was heated at 40, 80, or 120 °C for 60 min. After the heat treatment, the aroma components retained in the microcapsules were determined by the same method as described above.

Particle Size and Moisture Content Analysis of Spray-Dried Microencapsulated Model Mixtures. The spray-dried microencapsulated model mixtures were dispersed in 2-propanol. The size distributions were analyzed using a laser light scattering spectrophotometer (model SALD-2000, Shimadzu Corp., Ltd.), and the median diameter of the particles was obtained. The moisture contents of the microcapsules were determined according to the Karl Fischer method (Karl Fischer Titrator model KF-100, Mitsubishi Chemical Corp.).

Microscopy Observation of Microencapsulated Model Mixtures. *Surface Observation.* The microencapsulated model mixtures were placed on double-sided adhesive tape and observed with a SEM (model JSM-6301, JEOL, Ltd.) or an atomic force microscope (AFM; model SPA300, Seiko Instruments Inc.). The samples for the SEM observation were coated in advance with platinum using ion sputtering (model JFC-1300, JEOL, Ltd.). The SEM observations were made at 1000−10000× magnifications at an acceleration voltage of 5 kV.

Inner Structure Observation. Approximately 0.5 g of the microcapsules was mixed in a beaker with 15 g of epoxy resin (the trade name is EpoFix, Struers Corp.) and 2 g of hardener. Before they hardened, we placed the mixtures in aluminum foil dishes (ca. 50 mm in diameter) and held them in a decompression desiccator (ca. 2.5 kPa) for 5 min to remove small inner bubbles. After they had hardened (ca. 24 h after), the samples were snapped and the broken faces were observed with SEM by the same method as described above.

Statistical Analysis. The statistical analysis was carried out using statistical analysis software (SPSS 12.0J for windows, SPSS, Inc.). Tukey's HSD test was applied to determine significant differences among the quantities of retained aroma components. A significance level of $p < 0.05$ was applied.

RESULTS AND DISCUSSION

La France Pear Aroma Model Mixture. The volatile composition of La France pear was reported by Shiota (*33*). He has isolated its volatile components (36 kinds of volatile compounds) by simultaneous distillation and extraction and has reported their percentages. We have determined the key flavor components of La France pear by aroma extract dilution analysis (*34*). In this study, the key flavor components were determined by a GC−olfactometry method. Among the volatile components reported by Shiota, we mixed six components closely related to the pear aroma and prepared the La France pear aroma model mixture.

To evaluate the smell of the model, we carried out a sensory test. Eighteen percent of the panel members judged the test solution to be "extremely similar to La France pear aroma (score 1)", and 77 considered it to be "moderately similar to La France pear aroma (score 2)". Only 5% of the panel members rated the test solution as "different from La France pear aroma (score 3)". The average score was 1.9: The smell of the model mixture seemed to be moderately similar to that of La France pear juice.

Aroma Components Retained in Microencapsulated Model Mixtures. The median particle size and water content of the spray-dried microencapsulated model mixtures are shown in **Table**

Table 3. Aroma Components Retained in Spray-Dried Microcapsules[a]

	carrier solid			
	g/100 g[b] (%)			
compound	α-CD	GA	SSPS	HBCD
hexanal	0.07 ± 0.005 (1.0)	0.16 ± 0.003 (1.5)	0.15 ± 0.004 (1.3)	0.02 ± 0.001 (1.6)
propyl acetate	0.07 ± 0.001 (1.0) a	0.45 ± 0.008 (4.1) b	0.57 ± 0.010 (5.0) c	0.06 ± 0.005 (4.4) b
butyl acetate	1.71 ± 0.049 (26.6) a	4.29 ± 0.081 (39.1) b	4.36 ± 0.105 (38.3) b	0.57 ± 0.019 (42.1) c
3-methylbuthyl aceta	0.01 ± 0.001 (0.2)	0.02 ± 0.001 (0.2)	0.02 ± 0.001 (0.2)	0.00 ± 0.000 (0.1)
pentyl acetate	0.08 ± 0.008 (1.3)	0.24 ± 0.019 (2.2)	0.23 ± 0.015 (2.0)	0.01 ± 0.001 (1.0)
hexyl acetate	4.48 ± 0.427 (69.9) a	5.83 ± 0.676 (53.0) b	6.05 ± 0.358 (53.2) b	0.69 ± 0.039 (50.7) b
total	6.42 ± 0.487 (100.0) a	11.00 ± 0.772 (100.0) b	11.38 ± 0.475 (100.0) b	1.35 ± 0.615 (100.0) c

[a] Mean ± standard deviation ($n = 3$). Values in the row followed by the same letter are not significantly different ($p < 0.05$). Abbreviations are the same as in **Table 2**. [b] Aroma components (g)/dried microcapsule (100 g).

Table 4. Aroma Components Retained in Freeze-Dried Microcapsules[a]

	carrier solid			
	g/100 g[b] (%)			
compound	α-CD	GA	SSPS	HBCD
hexanal	0.10 ± 0.002 (1.0)	0.26 ± 0.019 (1.9)	0.14 ± 0.007 (1.4)	0.09 ± 0.003 (5.6)
propyl acetate	0.13 ± 0.003 (1.3) a	1.05 ± 0.031 (7.4) b	0.68 ± 0.005 (7.0) c	0.11 ± 0.001 (7.1) bc
butyl acetate	2.88 ± 0.038 (28.7) a	5.73 ± 0.074 (40.6) b	3.73 ± 0.121 (38.6) b	0.88 ± 0.011 (54.8) c
3-methylbuthyl aceta	0.03 ± 0.001 (0.2)	0.04 ± 0.002 (0.3)	0.02 ± 0.001 (0.2)	0.00 ± 0.000 (0.2)
pentyl acetate	0.22 ± 0.006 (2.2)	0.36 ± 0.041 (2.5)	0.19 ± 0.017 (1.9)	0.01 ± 0.001 (0.9)
hexyl acetate	6.67 ± 0.106 (66.5) a	6.66 ± 0.284 (47.3) b	4.94 ± 0.460 (50.8) b	0.50 ± 0.017 (31.4) c
total	10.03 ± 0.135 (100.0) a	14.09 ± 0.439 (100.0) b	9.71 ± 0.596 (100.0) a	1.60 ± 0.032 (100.0) c

[a] Mean ± standard deviation ($n = 3$). Values in the row followed by the same letter are not significantly different ($p < 0.05$). Abbreviations are the same as in **Table 2**. [b] Aroma components (g)/dried microcapsule (100 g).

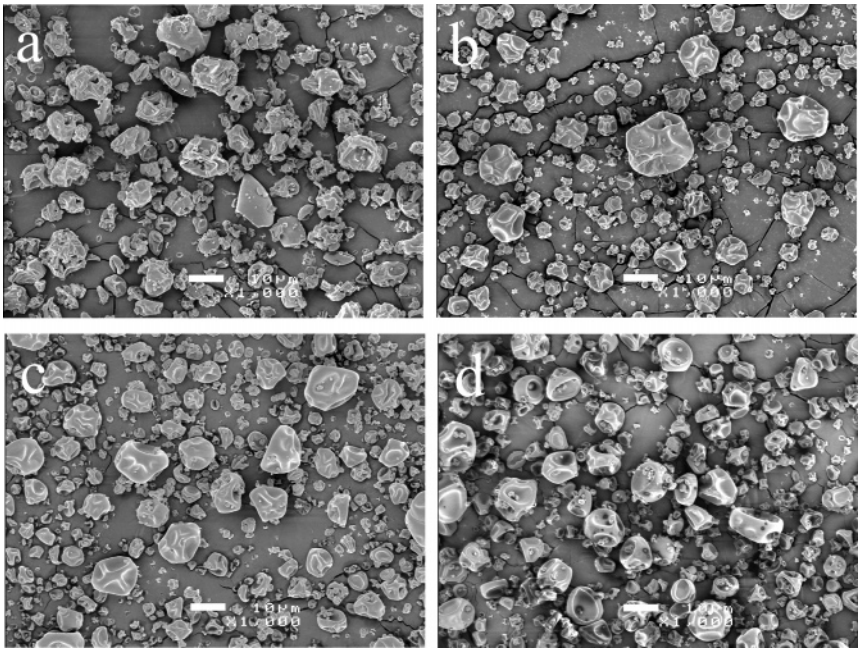

Figure 1. Scanning electron micrographs of spray-dried microcapsules with (**a**) α-CD, (**b**) GA, (**c**) SSPS, and (**d**) HBCD. Bars represent 10 μm. Abbreviations are the same as in **Table 2**.

2, and the retained aroma components are in **Table 3**. The particle sizes ranged from 8.34 μm for microcapsules with α-CD to 9.67 μm for microcapsules with SSPS. Their water contents ranged from 4.34% (w/w) for microcapsules with SSPS to 5.35% (w/w) for microcapsules with HBCD. The total aroma contents were significantly different except between GA and SSPS, depending upon the carrier solids. They ranged from 1.35 g/100 g of microcapsules for those with HBCD to 11.4 g/100 g for those with SSPS.

The aroma components retained in the freeze-dried microencapsulated model mixtures are provided in **Table 4**. The total aroma contents here also varied significantly except between α-CD and SSPS, depending upon the carrier solids. The values ranged from 1.60 g/100 g of microcapsules for those with HBCD to 14.1 g/100 g of microcapsules for those with GA. Thus, except for the microcapsules with SSPS, the freeze dry system retained more aroma components than the spray dry system ($p < 0.05$). This is because the aroma components are volatile (e.g.,

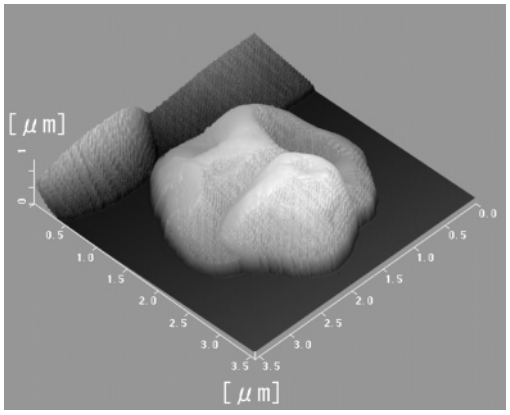

Figure 2. Atomic force micrograph of a spray-dried microcapsule with SSPS.

boiling points: butyl acetate, 125−126 °C; hexyl acetate, 169 °C) and some of them may vaporize away during high-temperature condition of the spray-drying process (drying temperature: inlet, 150 °C; outlet, 96 °C). The percentage of propyl acetate was significantly lower in the α-CD system (spray dried, 1.0%; freeze-dried, 1.3%) in comparison with that of the GA, SSPS, and HBCD systems (spray dried, 4.1−5.0%; freeze-dried, 7.0−7.4%). Similarly, the percentage of butyl acetate was also significantly lower in the α-CD system (spray dried, 26.6%; freeze-dried, 28.7%) than in that of the GA, SSPS, and HBCD systems (spray dried, 38.3−42.1%; freeze-dried, 38.6−54.8%). On the other hand, the percentage of hexyl acetate was significantly higher in the α-CD system (spray dried, 69.9%; freeze-dried, 66.5%) as compared with those of the GA, SSPS, and HBCD systems (spray dried, 50.7−53.2%; freeze-dried, 31.4−50.8%). We have previously studied the complexing abilities of α-, *β*-, or *γ*-CD with six kinds of acetate esters (the ethyl, propyl, butyl, pentyl, hexyl, and heptyl acetates) and reported that the complexing abilities of CDs were higher with the highly hydrophobic esters (e.g., hexyl acetate) and lower with the less hydrophobic esters (e.g., propyl acetate and butyl acetate) (*26*). Therefore, we attributed the results described above to the difference in complexing ability of the α-CD with the esters of the model mixture.

Microscopic Observation of Microencapsulated Model Mixtures. The SEMs of spray-dried microencapsulated model mixtures are shown in **Figure 1**. All of the microcapsules had highly dented surfaces; in particular, the surface of the microcapsule with α-CD was crumpled. It is possible that these dents were formed by the high degree of decompression occurring during the SEM observation (the pressure during the platinum coating was ca. 5 Pa; the pressure of the SEM observation was ca. 0.1 mPa) by the evaporation of the volatile compounds retained in the microcapsules. To clarify whether these dents formed for this reason, we observed the microcapsules with an AFM. In the case of the AFM observation, the samples were observed at atmospheric pressure without a platinum coating, so that sample deformation caused by decompression would not occur. The AFM results also exhibited many dents, similar to the SEM samples shown in **Figure 1**. For example, the atomic force micrograph of the spray-dried microcapsule with SSPS is provided in **Figure 2**. Apparently, the dents were not formed by the SEM observation decompression but were produced during the spray-drying process.

The SEMs of the cross-sections of the spray-dried microcapsules appear in **Figure 3**. The cross-sections comprise the area within the white dotted line ellipses; the area outside the ellipses is an epoxy resin. The shapes of the cross-sections varied depending upon the carrier solids. The microcapsules retained much of the aroma contents; the microcapsules with the SSPS and GA (total aroma contents: SSPS, 11.4 g/100 g of microcapsule; GA, 11.0 g/100 g of microcapsule) had a large number of small cavities inside the microcapsules. In contrast, the microcapsules retained just a little of the aroma contents: The microcapsule with the HBCD (total aroma contents: 1.35 g/100 g of microcapsule) had only a few small cavities inside the microcapsule. Several studies have been conducted on flavor microencapsulation by spray drying, and it has been recognized that the flavor components, in the form of small droplets, are found embedded in the wall matrix (*27*, *28*). Hence, it appears that the microcapsules with the SSPS and GA stored the most

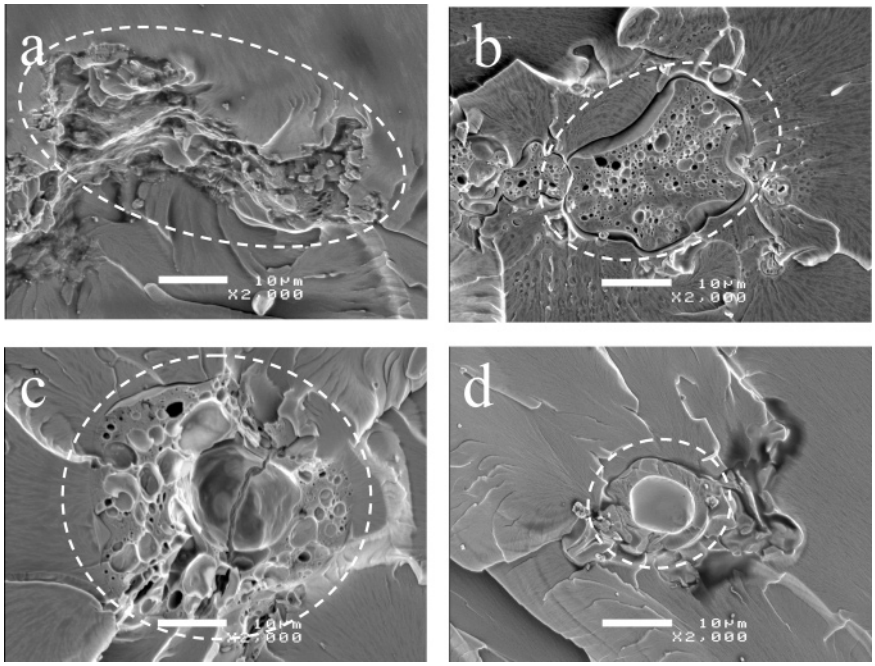

Figure 3. Scanning electron micrographs of cross-sections of spray-dried microcapsules with (**a**) α-CD, (**b**) GA, (**c**) SSPS, and (**d**) HBCD. The microcapsules are the areas inside the broken circles. Bars represent 10 *μ*m. Abbreviations are the same as in **Table 2**.

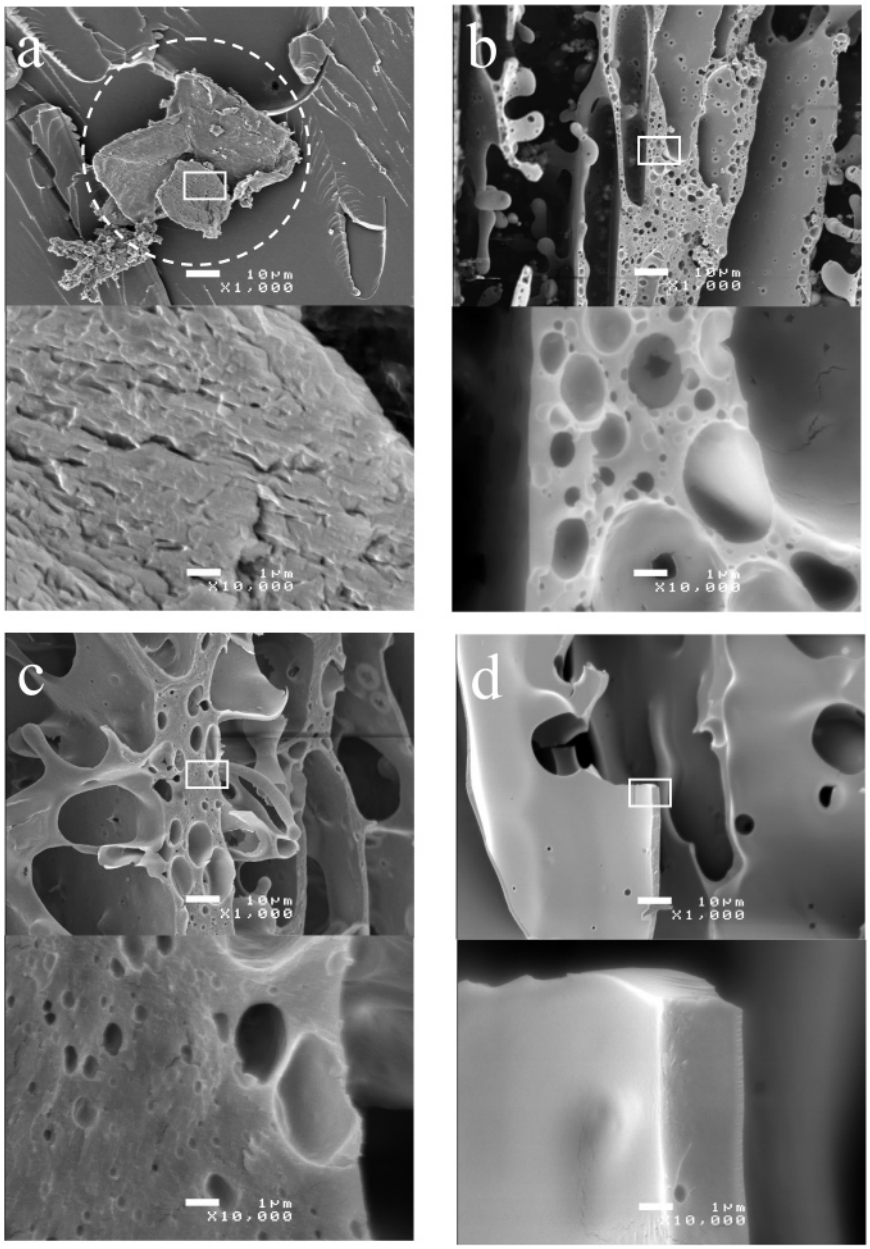

Figure 4. Scanning electron micrographs of cross-sections of bulk of freeze-dried microcapsules with (**a**) α-CD, (**b**) GA, (**c**) SSPS, and (**d**) HBCD. Bars represent 10 (upper images) and 1 μm (lower images). Abbreviations are the same as in **Table 2**.

aroma components in their wall matrix in the same manner. Some of the small cavities observed in their cross-sections seemed to be the traces of model mixture droplets. The solubility of the components of the model mixture is low [e.g., solubility in water: butyl acetate, 1.0% (w/w, 20 °C); hexyl acetate, insoluble]; therefore, most of the model mixture solution may disperse into an emulsion by homogenizing before drying. Then, the carrier solids seem to act as encapsulants during the drying process. On the other hand, although the microcapsule with the α-CD retained 6.42 g/100 g of microcapsule of the aroma components, no cavity was observed in the cross-section. In our previous paper (*26*), we reported that butyl acetate and hexyl acetate, the main compounds in the model mixture, are included in the α-CD cavity and form α-CD−ester complexes. Considering the results reported, the microcapsule with α-CD seemed not to store the aroma components in the form of small droplets embedded in the wall matrix but to hold them as α-CD inclusion complexes. We thus believe that the aroma retention mechanism of the microcapsules with α-CD is different from that of the microcapsules with SSPS and GA.

The SEMs of the cross-sections of the bulk of the freeze-dried microencapsulated model mixtures are given in **Figure 4**. Porous solids were formed after the freeze drying in the GA, SSPS, and HBCD systems. These were snapped, and their cross-sections were observed. However, a powder was formed after the freeze drying in the α-CD system. These powders were embedded in epoxy resin and snapped after hardening; then, their cross-sections were observed (by the same method as the case of **Figure 3**). The bulk of the microcapsules retained much of the aroma contents; the microcapsules with GA and SSPS (total aroma contents: GA, 14.1 g/100 g of microcapsule; SSPS, 9.71 g/100 g of microcapsule) had a large number of small cavities inside of them. In contrast, the bulk of the microcapsule retained little aroma contents; the microcapsule with HBCD (total aroma contents: 1.60 g/100 g of microcapsule) had a smooth surface with only a few small cavities. On the other

Table 5. Effect of Composition of Carrier Solid on the Aroma Components Retained in Freeze-Dried Microcapsules[a]

	g/100 g[b] (%)					
	composition of carrier solid					
GA (%, w/w)	100	80	60	40	20	0
compound α-CD (%, w/w)	0	20	40	60	80	100
hexanal	0.26 ± 0.019 (1.9)	0.16 ± 0.009 (1.7)	0.08 ± 0.010 (1.6)	0.11 ± 0.002 (1.6)	0.13 ± 0.002 (1.8)	0.10 ± 0.002 (1.0)
propyl acetate	1.05 ± 0.031 (7.4)	0.52 ± 0.011 (5.6)	0.18 ± 0.009 (3.5)	0.16 ± 0.006 (2.4)	0.19 ± 0.011 (2.6)	0.13 ± 0.003 (1.3)
butyl acetate	5.73 ± 0.074 (40.6)	3.56 ± 0.055 (38.4)	1.92 ± 0.029 (37.4)	2.00 ± 0.054 (30.5)	2.29 ± 0.051 (31.0)	2.88 ± 0.038 (28.7)
3-methylbuthyl acetate	0.04 ± 0.002 (0.3)	0.03 ± 0.003 (0.3)	0.02 ± 0.002 (0.4)	0.03 ± 0.002 (0.5)	0.04 ± 0.002 (0.6)	0.03 ± 0.001 (0.2)
pentyl acetate	0.36 ± 0.041 (2.5)	0.22 ± 0.021 (2.3)	0.12 ± 0.012 (2.2)	0.19 ± 0.010 (2.9)	0.26 ± 0.020 (3.5)	0.22 ± 0.006 (2.2)
hexyl acetate	6.66 ± 0.284 (47.3)	4.77 ± 0.257 (51.6)	2.81 ± 0.186 (54.9)	4.08 ± 0.116 (62.1)	4.47 ± 0.105 (60.5)	6.67 ± 0.106 (66.5)
total	14.09 ± 0.439 (100.0) a	9.26 ± 0.315 (100.0) b	5.12 ± 0.245 (100.0) c	6.58 ± 0.154 (100.0) d	7.38 ± 0.093 (100.0) e	10.03 ± 0.135 (100.0) f

[a] Mean ± standard deviation ($n = 3$). Values in the row followed by the same letter are not significantly different ($p < 0.05$). Abbreviations are the same as in **Table 2**. [b] Aroma components (g)/dried microcapsule (100 g).

Table 6. Aroma Components Retained in Spray-Dried Microcapsules after Heat Treatment[a]

	g/100 g[b] (%)					
	α-CD			GA		
compound	40 °C	80 °C	120 °C	40 °C	80 °C	120 °C
hexanal	0.08 ± 0.004 (1.2)	0.07 ± 0.002 (1.1)	0.07 ± 0.002 (1.0)	0.17 ± 0.010 (1.6)	0.16 ± 0.006 (1.6)	0.20 ± 0.007 (1.7)
propyl acetate	0.08 ± 0.005 (1.2)	0.07 ± 0.002 (1.1)	0.06 ± 0.002 (0.8)	0.46 ± 0.059 (4.4)	0.45 ± 0.020 (4.5)	0.48 ± 0.026 (4.3)
butyl acetate	1.70 ± 0.019 (26.2)	1.71 ± 0.028 (25.5)	1.58 ± 0.024 (24.3)	4.16 ± 0.202 (39.4)	4.07 ± 0.113 (40.4)	4.34 ± 0.157 (38.5)
3-methylbuthyl acetate	0.01 ± 0.001 (0.2)	0.01 ± 0.001 (0.2)	0.01 ± 0.001 (0.2)	0.03 ± 0.002 (0.3)	0.03 ± 0.001 (0.3)	0.03 ± 0.000 (0.2)
pentyl acetate	0.10 ± 0.008 (1.6)	0.10 ± 0.004 (1.4)	0.09 ± 0.001 (1.4)	0.25 ± 0.023 (2.3)	0.25 ± 0.015 (2.5)	0.26 ± 0.007 (2.3)
hexyl acetate	4.50 ± 0.173 (69.6)	4.74 ± 0.209 (70.7)	4.69 ± 0.138 (72.3)	5.48 ± 0.467 (52.0)	5.12 ± 0.183 (50.8)	5.96 ± 0.368 (52.9)
total	6.46 ± 0.175 (100.0) a	6.70 ± 0.235 (100.) a	6.49 ± 0.154 (100.0) a	10.53 ± 0.591 (100.0) b	10.07 ± 0.258 (100.0) b	11.27 ± 0.484 (100.0) b

[a] Mean ± standard deviation ($n = 3$). Values in the row followed bgy the same letter are not significantly different ($p < 0.05$). Abbreviations are the same as in **Table 2**. [b] Aroma components (g)/dried microcapsule (100 g).

hand, although the microcapsule with α-CD retained 10.0 g/100 g of microcapsule of aroma components, no cavity was observed. The small cavities shown in **Figure 4** closely resembled the images shown in **Figure 3**. From the discussion above, a reasonable interpretation for these results seemed to be that the microcapsules prepared by freeze drying and by spray drying retain the aroma components in the same manner.

Multiple Effects on Aroma Retention by Concomitant Use of α-CD and GA. In the previous section, we mentioned that the aroma retention mechanism for α-CD is different from that of GA and SSPS. Thus, a multiplier aroma retention effect might be expected by the concomitant use of α-CD and another carrier solid (GA or SSPS). Many investigations have been preformed to prepare microencapsulated flavors by concomitant use of different types of carrier solids (*2*, *10*, *11*, *13*, *14*, *28*, *32*). To this end, the α-CD and GA were mixed in various ratios (four levels) as carrier solids, and the freeze-dried microencapsulated model mixtures were prepared. The aroma components retained in them are shown in **Table 5**. The GA was used in this test, because the freeze-dried microcapsule containing it kept the highest amount of aroma components of all of the carrier solids (**Table 4**). The samples were prepared by freeze drying in this test, because the freeze-dried microcapsules retained more aroma components than the spray-dried microcapsules in the CD and GA systems. The total aroma components significantly decreased when the α-CD and GA were used together, and no multiplier effect for aroma retention was observed. The smallest amount of the total aroma components was observed in the system with the blend of GA 60% (w/w) + α-CD 40% (w/w), and they comprised about a third of those retained in the GA 100% (w/w) system or a half of those in the α-CD 100% (w/w) system. To investigate the cause of this effect, we observed

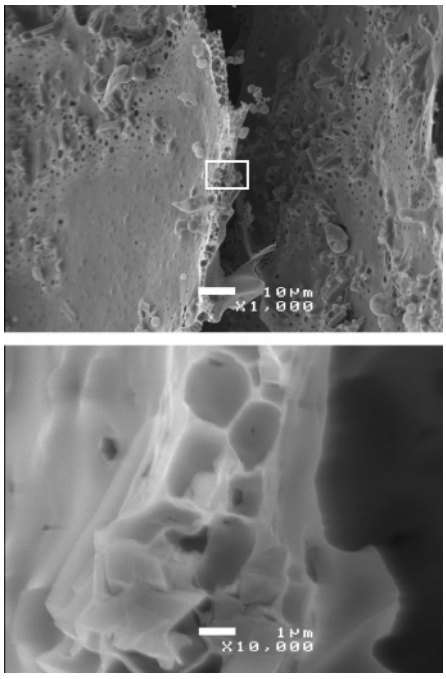

Figure 5. Scanning electron micrographs of cross-sections of a bulk freeze-dried microcapsule [GA 60% (w/w) + α-CD 40% (w/w)]. Bars represent 10 (upper images) and 1 μm (lower images).

the cross-section of the bulk of microcapsule [GA 60% (w/w) + α-CD 40% (w/w)] by SEM (**Figure 5**). The small cavities with diameters of <1 μm, as observed in **Figure 4b** [GA 100% (w/w) system], were not found. Therefore, we suggest that a decrease in the number of minute aroma mixture droplets

embedded in the wall matrix might contribute to the lowered aroma components retention. However, the elucidation of the mechanisms involved is a topic for the future.

Stability of Spray-Dried Microencapsulated Model Mixtures against Heat Treatment. The aroma components are highly volatile, and heat treatment will cause them to vaporize away. Therefore, when microencapsulated flavors are used as foodstuffs, their thermal stabilities for flavor retention are one of the most important factors. If their thermal stabilities are poor, the flavor components retained in them will be lost during storage in heat. In addition, microencapsulated flavors with sufficient thermal stability can allow heat sterilization. To obtain some basic data on the thermal stability of microencapsulated flavors, we subjected the microencapsulated model mixtures to heat treatments (at 40, 80, or 120 °C for 60 min) and then determined the retained aroma components (**Table 6**). The test temperature of 40 °C constituted the model condition for storage in heat. The test temperature of 120 °C was the sterilization condition for a common retorting process. Earlier, we mentioned that the mechanism for aroma retention using α-CD is different from that of the GA. Thus, their thermal stabilities might also be different; to discover if such was the case, we tested their stabilities. After the heat treatment, the total aroma components retained in the microcapsules with α-CD were 6.46−6.70 g/100 g of microcapsules. There were no significant differences between heated and unheated samples (unheated sample, 6.42 g/100 g of microcapsule). The totals retained in the microcapsules with GA after heat treatment were 10.1−11.3 g/100 g of microcapsules. There were also no significant differences between heated and unheated samples (unheated sample, 11.0 g/100 g of microcapsule). The microcapsules with α-CD and GA seemed to be thermostable under a nitrogen gas flow.

In conclusion, eight types of microcapsules of La France pear aroma model mixture were prepared. The amount of aroma components retained in microcapsules varied depending upon the carrier solids used (four types) and the drying methods (spray dry or freeze dry). Analysis of the percentage of retained aroma components and SEM observations of the cross-sections of microcapsules showed that the aroma retention mechanism of the microcapsule with α-CD seemed to be different from that of the microcapsules with the other carrier solids: In the α-CD system, aroma components are retained as the inclusion complexes, while in the GA or SSPS systems, they are retained as small droplets embedded in the wall matrix. The microcapsules containing α-CD and GA were thermally stable under a nitrogen gas flow.

NOTE ADDED AFTER ASAP PUBLICATION

The original posting of June 13, 2006 contained an incorrect version of Tables 3 and 4. The correct version is shown in the posting of June 22, 2006.

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