

# Production and Properties of Spray-dried *Amaranthus* Betacyanin Pigments

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**Abstract:** *Amaranthus* betacyanin extracts were spray-dried using a range of maltodextrins [10–25 dextrose equivalent (DE)] and starches (native/modified) as carrier and coating agents at 5 inlet/outlet air temperatures and 4 feed solid contents. Higher inlet/outlet air temperatures caused greater betacyanin loss during spray drying, and affected slightly the pigment stability during storage. Adding maltodextrins and starches significantly reduced the hygroscopicity of the betacyanin extracts and enhanced storage stability. The 25 DE/10 DE mixed powders provided a longer predicted half-life (63.6 wk) compared to the 25 DE and the 10 DE powders separately. The best dried pigment-containing powder made was superior to commercial red beet powder in physical properties.

**Key words:** Spray drying, *Amaranthus*, betacyanins, food colorants

## Introduction

AN INCREASING TREND IN THE FOOD INDUSTRY IS TOWARD replacement of synthetic colorants with natural pigments. *Amaranthus* pigments are red-violet betacyanins, like the red beet pigments that are extensively used worldwide (Schnetzler and Breene 1994; Hendry and Houghton 1996). *Amaranthus* betacyanins were identified as amaranthine and isoamaranthine (Piattelli and others 1964; Cai and others 1998b). The major betacyanins in red beets were identified as betanin and isobetanin (Jackman and Smith 1996). They have the same basic structure (betanidin). *Amaranthus* pigments, representing a new source of betacyanin type pigments, could have large commercial potential to be developed as natural food colorants (Cai and others 1998b). Selected *Amaranthus* genotypes had much higher biomass and higher betacyanin content than others, and the pigments extracted from them had bright color characteristics with favorable stability under selected conditions (Cai and others 1998a). Moreover, these betacyanin pigments were successfully tested in jelly, higher pH beverages, and ice cream (Cai and Corke 1999). *Amaranthus* pigments can be legally used as food ingredients in China (Cai and others 1998a), and we understand that such water-extracted pigments would also be legal in the United States. In our experience, there are no adverse flavor or odor characteristics of *Amaranthus* pigments, and the high protein content of crude extracts (Cai and others 1998a) may be nutritionally favorable.

Most natural plant pigments, including betacyanins and anthocyanins, are easily affected by temperature, oxygen, light and water activity. Freeze drying is considered to be the best way to dry sensitive plant pigments. However, spray drying, if feasible, would be a more practical and economical method of producing powdered sensitive colorants as the processing cost is 30 to 50 times less than for freeze drying. Spray drying is also the most common method of drying for encapsulation, to entrap a sensitive ingredient in a coating material or "wall" for isolation from the environment and to protect against oxidation (Masters 1985; Desobry and others 1997; Francis 1999). Main and others (1978) reported spray drying anthocyanin concentrates for use as food colorants. There are many reports about spray drying and encapsulation of carotenoids (Beatus and others 1985; Wagner and Warthesen 1995; Desobry and others 1997). However, no reports were found on spray drying of *Amaranthus* betacyanins.

Gum arabic, dextrose, sugar, starches, gelatin, methyl cellulose, gum tragacanth and mixtures of these have been used as carrier and coat agents for the spray drying of flavors and colo-

rants (Glicksman 1969; Revie and Thomas 1972; Anonymous 1973; Main and others 1978; Francis 1986). Maltodextrins (hydrolyzed starches) were effective encapsulating agents when used in the spray drying of sensitive flavors and carotenoids (Wagner and Warthesen 1995; Desobry and others 1997). Maltodextrins were also a good compromise between cost and effectiveness, were bland in flavor, had low viscosity at high solids ratio, and were available in different average molecular weights (DEs: 4, 10, 15, 20, 25, 30, and 42). Various carrier agents could provide different protection against oxidation since they create different wall thicknesses and densities of the spray-dried powder particles. However, no previous work on hydrolyzed starches and modified starches as carrier agents for spray drying of *Amaranthus* betacyanins was reported.

Our objectives were 1) to investigate the spray drying of *Amaranthus* pigment extracts, 2) to elucidate the effects of various carrier agents, and 3) to evaluate the properties of different spray-dried pigment powders and their storage stability. The results of this study would be helpful in developing economical commercial processes for spray-dried betacyanin extracts as powdered foodgrade colorants.

## Materials and Methods

### Materials

Fresh *Amaranthus* plant material for pigment extraction. Superior *Amaranthus* pigment genotypes (Cr072, Japan19, San154, Beijing Red) were selected in earlier field experiments in 1995 and 1996 in Wuhan, China (Cai and others 1998b). Fresh samples (about 25 kg) of inflorescences (Cr072, Japan19), seedlings and leaves (San154, Beijing Red) were grown in 1998 and 1999, harvested, washed, and cleaned in Wuhan, and were kept frozen at  $-18^{\circ}\text{C}$  in plastic bags in Hong Kong until further extraction.

Carrier agents for spray drying. Maltodextrins (10, 20, and 25 DE) were from Sigma Chemical Co., St. Louis, Mo., U.S.A.; 15 DE was from Amylum Group, Aalst, Belgium. Maize starch was purchased from Sigma Chemical Co. Modified starch (phosphorylated waxy maize starch) was made in our lab (Liu and others 1999) (commercial modified starch was not used to ensure control over the processing).

Spray-dried red beet powder (ck). Red beet powder (No. 3600/E162 Beet Powder) was obtained from Warner-Jenkinson Co., Inc. (St. Louis, Mo., U.S.A.).

### Extraction of *Amaranthus* pigments

Aqueous extracts of *Amaranthus* pigments were prepared following Cai and others (1998b) with modification: thaw frozen materials → cut into small pieces → add twice volume of water → blanch and extract in a hot water bath (80 °C, 3 min) → quickly cool on an ice bath → centrifuge → concentrate → pigment concentrate (solid content about 6%).

### Drying method

Preparation of feed mixtures. Carrier agents (maltodextrin 10, 15, 20, 25 DE; starches) were combined with the pigment concentrate and stirred to homogeneity for the feed mixtures. Ascorbic acid was added to the feed mixtures to adjust to pH 5.6-6.0. For comparing carrier agents and spray drying temperatures, the final feed mixtures were controlled to 20% total solids. For evaluating different levels of carrier agent (maltodextrin 15 DE), 4 levels of the feed mixture used were: 10.5%, 19.8%, 30.0% and 39.2% solids. Solid contents were measured using a PR-100 digital refractometer (Atago Co., Ltd., Japan). One liter to about 4 liters of feed mixtures were prepared for the purposes of different experiments.

**Spray drying.** The feed mixtures were spray-dried in a Lab-Plant SD-05 spray drier (Lab-Plant Ltd., England) with main spray chamber (500 mm long × 215 mm). The drier was operated according to the conditions in Table 1. The feed mixtures containing starch (native or modified) were constantly stirred to ensure feed homogeneity during spray drying.

**Freeze drying.** Freeze drying was conducted for comparison with spray drying. The feed mixtures were frozen in liquid N<sub>2</sub> and freeze-dried in a Heto FD3 freeze dryer (Heto-Holten A/S, Denmark) for 24 h. The dried mixture was ground to powder.

### Pigment powder storage

Pigment powders were stored in 70 mL plastic cups sealed with screw caps, placed in a large sealed plastic container with 1 kg silica gel. Characteristics at zero storage time were analyzed within 1 d after drying. For storage stability analysis, Petri dishes (90 mm dia, 15 mm ht) were filled with sample (about 3 g) to expose a large surface area to air during storage. The dishes were stored at 25 °C in 2 airtight plastic containers (40 × 20 × 25-cm) filled, respectively, with MgCl<sub>2</sub> saturated solution (32% RH) and with 2 kg silica gel (about 5% RH) for 16 wk. Samples for pigment degradation kinetic analysis were stored in a 32% RH container filled with oxygen at 25 °C for 16 wk. Duplicate samples were used for each measurement.

### Measurement and calculation of experimental parameters

**Moisture and hygroscopicity.** Moisture (%) of pigment powders was determined by air oven method 945.14 (AOAC 1990). For hygroscopicity, samples (about 2 g) of each powder from the Petri dishes were placed at 25 °C in an airtight plastic container (40 × 20 × 25-cm) filled with Na<sub>2</sub>SO<sub>4</sub> saturated solution (81% RH). After 1 wk, hygroscopic moisture (hygroscopicity) was weighed and expressed as g of moisture per 100 g dry solids (g/100 g).

**Drying ratio, drying rate and productivity.** Drying ratio, drying rate and productivity for spray drying were calculated according to King (1985) and Masters (1985), slightly modified. Drying ratio =  $(T_o + 1) / (T_f + 1)$ , where T<sub>o</sub> is feed moisture (dry basis), and T<sub>f</sub> is powder moisture (dry basis). Drying ratio was calculated by (powder solid content / feed solid content). Productivity (g/h) = feed rate (g/h) / drying ratio. Drying rate (g/h) = feed rate - productivity. Slight loss of feed mixture on the wall of main spray chamber and of powders in the exhaust tube was neglected.

**Table 1—Operating conditions for spray drying of *Amaranthus* pigments**

| Drying air temperature |             | Feed rate<br>(g/h) |
|------------------------|-------------|--------------------|
| inlet (°C)             | outlet (°C) |                    |
| 150 ± 2                | 87 ± 4      | 390                |
| 165 ± 2                | 92 ± 4      | 425                |
| 180 ± 2                | 96 ± 5      | 460                |
| 195 ± 2                | 105 ± 5     | 495                |
| 210 ± 2                | 115 ± 5     | 530                |

Air-flow rate (m<sup>3</sup>/hr) 56 ± 2; compressor air pressure (bar) 1.4 – 1.5

**Bulk density.** Bulk density of powders was measured by weighing 10 g of sample and placing into a 100 mL graduated cylinder. A steady vibration was conducted on a vibrator for 3 min (Main and others 1978). The volume was then recorded and used to calculate bulk density as g/mL.

**Color parameters.** L\*, a\*, b\* were determined by a colorimeter (Chroma Meter CR-301, Minolta Co., Osaka, Japan). H<sup>o</sup> (Hue angle) indicates sample color, calculated as  $H^o = \tan^{-1}(b^*/a^*)$ .

**Glass transition.** Samples of spray-dried pigment powders were equilibrated at 25 °C and 32% RH (MgCl<sub>2</sub> saturated solution) for 1 wk. Glass transition temperature (T<sub>g</sub>) was determined by a differential scanning calorimeter (2920 MDSC, TA Instruments, Inc., Newcastle, Del., U.S.A.). The temperature range was from 20 °C to 100 °C with a heating rate of 5 °C/min (Desobry and others 1997). Five milligrams powder was weighed directly into a DSC sample pan and sealed. An empty pan was used as a reference.

**Betacyanin content.** Pigment content was measured with a Spectronic Genesys 5 spectrophotometer (Milton Roy, Ivyland, Pa., U.S.A.), expressed as absorbance value (E<sub>1cm</sub><sup>1%</sup> 536 nm) or % amaranthine and % betanin. The pigment powder samples (W 5 about 0.1 g) were accurately weighed into 100 mL volumetric flasks and McIlvaine's buffer (pH 5.6) was added to 100 mL. Absorbance values (A) of the pigment solutions were recorded at 536 nm in 1.0 cm path length quartz cuvettes. Percent amaranthine and % betanin of spray-dried pigment powder were calculated by the formulas:  $(A \times 10^2) / (W \times E_{1cm}^{1\%} 536 \text{ nm})$ , where E<sub>1cm</sub><sup>1%</sup> 536 nm was absorptivity for betacyanin, 779 nm for amaranthine and 1120 nm for betanin (Piattelli and others 1969; Hendry and Houghton 1996).

**Drying loss of pigment.** Drying loss of pigment (%) was analyzed at zero storage time, and calculated by the formula: (betacyanin content of spray-dried samples) × 100 / (betacyanin content of freeze-dried samples).

**Storage stability.** Pigment retention (%) was calculated by the formula: (betacyanin content at X storage time) × 100 / (betacyanin content at zero storage time). Rate constant (k) and half-life time (t<sub>1/2</sub>) were calculated by the method of Cai and others (1998a) using the regression analysis of ln (pigment retention) against storage time when plotted on a natural logarithmic scale.

**Scanning electron microscopy (SEM).** Particle structures of the powder microcapsules were evaluated with a Cambridge SEM 360 (S360) (Leica Cambridge Ltd., Cambridge, England). The powders were attached to SEM stubs using a 2-sided adhesive tape. The specimens were coated with gold-palladium, and examined on the S360 operated at 20 kV.

## Results and Discussion

### Drying rate, powder moisture and productivity for spray drying

High productivity of pigment powder with low moisture is important in spray drying. Inlet-air temperature used was from 150 °C to 210 °C (Table 1). Under the same airflow rate and compressor air pressure, outlet-air temperature (87 – 115 °C) and

**Table 2—Effect of spray drying temperature and feed solid content on drying rate, productivity and characteristics of *Amaranthus* pigment powders<sup>a</sup>**

| Inlet-air temperature (°C) <sup>b</sup> | Feed solid content (%) | Powder moisture (%) | Drying ratio | Drying rate (g/hr) | Productivity (g/hr) | Bulk density (g/ml) | Hygroscopic moisture (g/100g) | Drying loss of pigment (%) | Retention of pigment at 16 wk (%) <sup>c</sup> |
|---|------------------------|---------------------|--------------|--------------------|---------------------|---------------------|-------------------------------|----------------------------|--|
| 150                                     | 19.8                   | 6.80±0.60           | 4.71         | 306.8              | 82.8                | 0.67±0.010          | 46.0                          | 2.77±0.17                  | 88.2±0.8                                       |
| 165                                     | 19.8                   | 4.53±0.75           | 4.82         | 336.6              | 88.1                | 0.63±0.007          | 45.4                          | 3.85±0.18                  | 88.6±0.6                                       |
| 180                                     | 19.8                   | 2.88±0.21           | 4.91         | 366.1              | 93.8                | 0.58±0.010          | 49.2                          | 4.14±0.30                  | 86.7±1.3                                       |
| 195                                     | 19.8                   | 1.98±0.18           | 4.95         | 395.1              | 100.0               | 0.54±0.015          | 48.5                          | 6.08±0.37                  | 84.2±0.6                                       |
| 210                                     | 19.8                   | 2.13±0.34           | 4.94         | 423.0              | 107.3               | 0.52±0.008          | 48.2                          | 7.66±0.51                  | 84.5±1.0                                       |
| 180                                     | 10.5                   | 1.95±0.00           | 9.34         | 410.7              | 49.2                | 0.55±0.015          | 49.5                          | 5.31±0.47                  | 84.8±1.0                                       |
| 180                                     | 30.0                   | 3.67±0.56           | 3.21         | 316.7              | 143.2               | 0.63±0.008          | 45.3                          | 3.96±0.61                  | 88.6±1.3                                       |
| 180                                     | 39.2                   | 3.24±0.62           | 2.47         | 273.6              | 186.3               | 0.64±0.010          | 44.6                          | 3.73±0.17                  | 89.8±0.7                                       |
| Freeze drying (ck1)                     | 19.8                   | 1.25±0.08           | —            | —                  | —                   | —                   | 50.7                          | 0.00                       | 87.6±0.6                                       |
| Freeze drying (ck2)                     | 6.0                    | 5.67±0.80           | —            | —                  | —                   | —                   | 118.3                         | —                          | 77.3±0.6                                       |
| LSD ( $P < 0.05$ ) <sup>d</sup>         | —                      | —                   | —            | —                  | —                   | 0.025               | 3.4                           | 0.96                       | 2.1  |

<sup>a</sup> Feed solutions for spray drying were made from pigment extracts and 15 DE maltodextrin.

<sup>b</sup> ck1 with 15 DE maltodextrin, ck2 (pure betacyanin extracts) without adding maltodextrins.

<sup>c</sup> Powder samples stored at 25 °C and 32% RH.

<sup>d</sup> Least significant difference for comparison of means in the same column.

feed rate (390 – 530 g/h) rose with the increase of inlet-air temperature. Higher drying air temperature usually resulted in faster drying (higher drying rate) and higher powder productivity. Increased drying rates caused decrease of powder moisture. As inlet-air and outlet-air temperature rose, drying rate increased from 307 g/h to 423 g/h, and powder productivity increased from 83 g/h to 107 g/h, but powder moisture decreased from 6.8% to 2.1% (Table 2). Similar trends were observed by Main and others (1978), King (1985), and Fu and Etzel (1995). It was also found that increasing feed solid content (10.5% → 39.2%) could raise powder productivity significantly at the same airflow rate, compressor air pressure and inlet-air temperature (180 °C) (Table 2), which could reduce production cost.

### Powder properties

The bulk density of pigment powders decreased with the increase of spray drying air temperature (Table 2). The higher drying rate obtained at higher drying temperature probably produced the higher ratio of surface-to-volume for the spray-dried capsules, and caused the lower bulk density of the powders. The lower the bulk density, the more occluded air within the powders, and therefore, there was a greater possibility for oxidative degradation of the pigments and reduced storage stability. The bulk density of different levels of maltodextrin 15 DE in the feed increased as the feed solid levels increased. Pure betacyanin pigment powders easily absorbed moisture because the betacyanin molecule has many hydrophilic groups (Piattelli and others 1964; Huo and Guo 1994). The hygroscopic moisture of spray-dried betacyanin powders with 15 DE maltodextrin at various drying temperatures ranged from 45.4 g/100 g to 49.2 g/100 g (Table 2). Their average value was only 47.5 g/100 g, significantly lower than the hygroscopic moisture of the betacyanin powder (118.3 g/100 g) without added maltodextrin. This indicated that maltodextrin as a carrier and coating agent could reduce the hygroscopicity of the betacyanins. It was observed that the spray-dried powders with maltodextrin had better solubility and dispersibility, although these factors were not investigated in detail in this study.

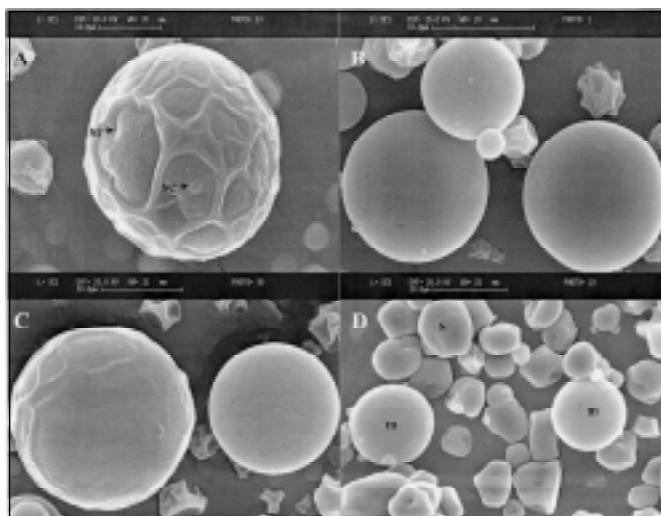
### Particle size and microstructure

Examination of SEM micrographs showed that the particle size of spray-dried betacyanin powders ranged from 5 μm to 40 μm approximately. Particle size decreased with increase of spray drying air temperatures, or with decrease of feed solid levels. These results coincided with the changes in bulk density. The outer topography of the spray-dried capsules was affected by wall composition (Figure 1A-D). Structural analysis revealed there were many more surface indentations and cracks in wall systems containing lower DE maltodextrins than in those con-

taining higher DE maltodextrins. Most of the spray-dried capsules containing 25 DE maltodextrin looked like smooth spheres, with hardly any surface cracks in the wall systems. This confirmed reports of Anandaraman and Reineccius (1986) and Wagner and Warthesen (1995) regarding the protection against core oxidation provided by higher DE maltodextrins. Different outer structures could directly explain the effect of various carrier and coating agents on properties and stability of the betacyanin powders (see the following related section).

### Pigment loss during spray drying and pigment retention during storage

The spray drying process, compared to the freeze drying process, led to a 2.77% degradation of betacyanin pigments at 150 °C, 3.85% at 165 °C, 4.14% at 180 °C, 6.08% at 195 °C and 7.66% at 210 °C (Table 2). This revealed that higher inlet-air and outlet-air temperature caused more pigment losses. Thus, higher drying temperature (> 180 °C) is not suitable for spray drying of betacyanins, though it can give higher drying rate and higher productivity. In the following discussion, these drying losses were not considered and 100% retention corresponds to the amount of betacyanin in each powder at zero storage time. After



**Figure 1—Typical micrographs of microcapsules of spray-dried betacyanin powders containing various carrier and coating agents: (A) 10 DE, (B) 25 DE, (C) 25 DE/10 DE (3:1) maltodextrin, and (D) modified corn starch. m – microcapsule, s – starch granule, sc – surface crack and si – surface indentation. Spray drying conditions: inlet/outlet temp 180 °C/96 °C, feed rate about 460 g/h, total feed solid content 20.5 % (betacyanin solids 6%).**

16-wk storage at 25 °C and 32% RH, the pigment retention of the spray-dried powder samples seemed to decrease slowly with increase of drying air temperature (Table 2). This implied that spray drying air temperature affected the storage stability of the betacyanin powders, because the higher the drying air temperature, the lower the bulk density of the powders. Table 2 also showed that pigment retention of the powders by spray drying below 180 °C was similar to that of the freeze-dried powders during storage. The betacyanin extracts without adding carrier agents gave the lowest pigment retention at 32% RH and 25 °C.

Higher solid content in the in-feed material not only raised the spray-dried powder productivity and reduced the production cost, but also led to less betacyanin loss during spray drying (Table 2). Furthermore, the betacyanin retention of the spray-dried powder during storage increased slightly as levels of maltodextrin 15 DE increased. The favorable effect of decreased degradation rate with increased proportion of carrier may be due to a corresponding decrease in surface betacyanins in the capsules. Moreover, at higher in-feed solids, the particle size usually increased, the total surface area decreased, and the bulk density increased (Bhandari and others 1992). However, too high a feed solid content could increase the feed viscosity and cause more solids to paste on the wall of main spray chamber.

**Effect of carrier agents on properties and stability**

Hydrolyzed starches (maltodextrin 10, 15, 20, and 25 DE) and native or modified starches were used as the carrier agents in spray drying. The glass transition temperature ( $T_g$ ) of the spray-dried powders decreased as molecular weights of carrier agents decreased (Table 3).  $T_g$  of native and modified starches was the highest.  $T_g$  of maltodextrins (10 to 25 DE) ranged from 54.7 °C to 45.4 °C. Nevertheless, the hygroscopic properties of the spray-dried powders increased with the decrease of molecular weights of carrier agents. The hygroscopicity of 25 DE maltodextrin was the strongest (69.4 g/100 g). Lower  $T_g$  of carrier agents caused higher hygroscopicity of the spray-dried powders, because lower molecular weight maltodextrins contained shorter chains and more hydrophilic groups.

The betacyanin retention during storage of spray-dried powders with various carrier agents were compared (Table 3). At low humidity (5% RH) and 25 °C, the pigment retention with various maltodextrins after 16 wk storage was high (93.4 to 97.3%), and tended upwards as DE values increased. The results were similar to those for spray-dried carotenes (Wagner and Warthesen 1995). Various carrier agents created different wall densities to provide protection against oxidation of the encapsulated betacyanins. Lower DE maltodextrins might produce a very high degree of surface indentation and cracking, and cause the wall systems to be more permeable to oxygen (Figure 1A). Higher DE maltodextrins could form more dense and more oxygen impermeable wall systems (Figure 1B) providing better storage stability for pigments. Hence, 25 DE maltodextrin gave the highest pigment retention under the storage conditions used.

All carrier agents at 32% RH and 25 °C reduced the pigment retention compared to 5% RH and 25 °C (Table 3). At 32% RH, the pigment retention (88.7 to 83.7%) of various maltodextrins after 16-wk storage tended to decrease as the DE values increased. The results may be explained by the hygroscopicity of the carrier agents. The hygroscopicity of all spray-dried powders increased at higher humidity. Average moisture content of all spray-dried powders reached 7.4% at 32% RH after 10 d storage, significantly higher than initial average moisture content (3.4%). Water activity of pigment powders was one of most important factors affecting betacyanin stability (Pasch and von Elbe 1975; Jackman and Smith 1996; Cai and others 1998a). The 20 DE and 25 DE maltodextrin had lowest pigment retention because of their higher hy-

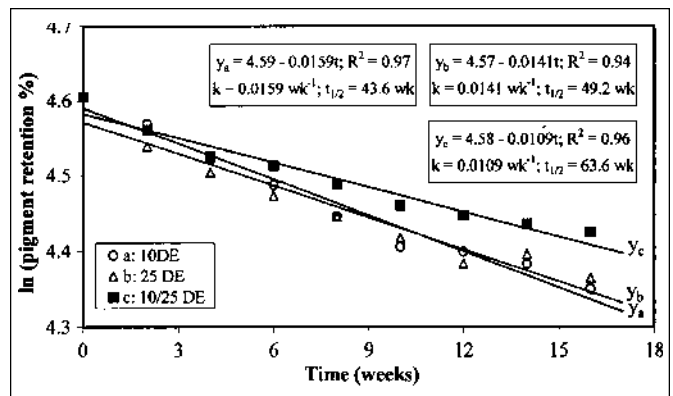
**Table 3—Effect of various carrier agents on properties and stability of spray dried pigment powders<sup>a</sup>**

| Carrier agents                  | Hygroscopicity (g/100g) | $T_g$ (°C) | Pigment retention at 16 wk (%) <sup>b</sup> |          |
|---------------------------------|-------------------------|------------|---|----------|
|                                 |                         |            | 5% RH                                       | 32% RH   |
| 10 DE maltodextrin              | 40.9                    | 54.7±1.0   | 93.8±1.0                                    | 88.7±0.7 |
| 15 DE maltodextrin              | 47.2                    | 52.3±1.2   | 93.4±0.8                                    | 86.0±0.8 |
| 20 DE maltodextrin              | 58.1                    | 49.7±0.8   | 94.6±0.6                                    | 83.7±0.6 |
| 25 DE maltodextrin              | 69.4                    | 45.4±1.0   | 97.3±0.6                                    | 84.2±1.1 |
| 10 DE : 25 DE (1:3)             | 51.5                    | 50.5±1.3   | 96.6±1.0                                    | 88.1±1.8 |
| Corn starch                     | 24.6                    | 60.5±0.4   | 89.2±1.2                                    | 79.7±1.3 |
| Modified corn starch            | 28.3                    | 58.0±0.8   | 91.6±0.8                                    | 84.5±1.3 |
| LSD ( $P < 0.05$ ) <sup>c</sup> | 2.5                     | 1.9        | 1.4   | 2.2      |

<sup>a</sup> Spray drying conditions: inlet temp 180 °C, outlet temp 96 °C, feed rate about 460 g/hr, feed solid content 20.5%.  
<sup>b</sup> Pigment powders were placed in Petri dishes stored in 5% RH (silica gel) or 32% RH (air-tight container) at 25 °C.  
<sup>c</sup> Least significant difference for comparison of means in the same column.

groscopicity at 32% RH.

Although 25 DE maltodextrin provided the best pigment retention, it produced stronger hygroscopicity at higher humidity causing the faster degradation of the betacyanins. Maltodextrin of 10 DE, with the lowest hygroscopicity, was mixed with 25 DE maltodextrin (25:10 = 3:1) in order to improve overall hygroscopicity. Capsules containing 25 DE/10 DE maltodextrin had smooth outer structures, similar to those containing 25 DE maltodextrin (Figure 1B-C). Differences of pigment retention of spray-dried powders with 10 DE, 25 DE and 25 DE/10 DE maltodextrins at 5% or 32% RH and 25 °C were limited since the results were obtained in an airtight container (not enough oxygen) (Table 3). Therefore, we also studied the pigment degradation kinetics of the above 3 powders in a 32% RH container filled with oxygen at 25 °C for 16 wk (Figure 2). Regression of ln (pigment retention %) against storage time was linear with negative slope when plotted on a natural logarithmic scale, indicating the degradation of the betacyanins followed first-order kinetics. Previous researchers (von Elbe and others 1974; Saguy and others 1978; Cai and others 1998a) reported similar results. The 25 DE/10 DE mixed sample had a much lower rate constant ( $k = 1.09 \times 10^{-2} \text{ wk}^{-1}$ ) and longer half-life value ( $t_{1/2} = 63.6 \text{ wk}$ ) than the 25 DE sample and the 10 DE sample alone (Figure 2). Thus, the combination between higher and lower DE maltodextrins as carrier agents could provide better stability to the spray-dried pigment powder. This was likely due to the interaction between the 2 maltodextrins to enhance the protection against oxidation and to improve the hygroscopicity of the powders. As far as we are aware, this is the first report on the interaction between various maltodextrins as mixed carrier agents in spray drying. The ratio between higher



**Figure 2—Degradation of *Amaranthus* betacyanin in spray-dried powders with (a) 10 DE, (b) 25 DE, and (c) 10/25 DE (1:3) maltodextrins in a 32% RH container filled with oxygen at 25 °C.**

**Table 4—Comparison of *Amaranthus* pigment powder and commercial beet powder (No. 3600)<sup>a</sup>**

| Spray-dried powder | Betacyanin content <sup>b</sup><br>(%) | Powder moisture<br>(%) | Hygroscopic moisture<br>(g/100g) | Color parameters <sup>c</sup> |       |       |                | Pigment retention <sup>d</sup><br>(%) |
|--------------------|--|------------------------|----------------------------------|-------------------------------|-------|-------|----------------|---------------------------------------|
|                    |  |                        |                                  | L*                            | a*    | b*    | H <sup>o</sup> |                                       |
| <i>Amaranthus</i>  | 0.74                                   | 3.08±0.24              | 48.5                             | 49.35                         | 32.60 | -2.47 | 355.7 (-4.3)   | 87.9±1.8                              |
| No. 3600 (E162)    | 0.31                                   | 4.96±0.39              | 58.8                             | 51.54                         | 19.64 | 0.71  | 2.0            | 84.3±1.4                              |

<sup>a</sup> *Amaranthus* pigment powder made by spray drying at 180 °C inlet temp using 19.8% solids in feed mixture, which contained pigment concentrate (6% solids) and 15 DE maltodextrin. No. 3600 was spray-dried beet powder with maltodextrin.

<sup>b</sup> Calculated as % amarantothine and % betanin.

<sup>c</sup> L\*, a\* and b\* values were means of triplicate determinations.

<sup>d</sup> Determined at 25 °C and 32% RH after 16 wk storage.

and lower DE maltodextrin requires further optimization. SEM examination revealed the outer structures of the capsules containing 25 DE/10 DE maltodextrins were almost smooth spheres on the whole, only with quite low extent of surface indentations in the wall systems (Figure 1C), little different from the 25 DE maltodextrin result.

Native corn starch and modified corn starch as carrier agents, compared to maltodextrins, improved the hygroscopicity of the spray-dried powders since they had much higher T<sub>g</sub> (60.5 °C and 58.0 °C) (Table 3). Nevertheless, the pigment retention of the spray-dried powders with native or modified starch was lower than that of those with maltodextrins at 5% or 32% RH and 25 °C. The reason might be that native or modified starch could not create dense and thick wall systems to protect against oxidation of the betacyanins. The particles observed by SEM were mainly the starch granules with only a few microcapsules (Figure 1D). Most of the betacyanin pigments probably attached to the surface of the starch granules. It was found that modified starch provided higher pigment retention than native starch (Table 3). The presence of negative charges on the modified starch molecules (phosphorylated waxy corn starch) may explain the high pigment retention. Certain modified starches might be used as reasonable absorptive supports for betacyanin pigments in the food industry.

### Comparison between *Amaranthus* betacyanin powder and commercial pigment powder (No. 3600/E162)

Red beet pigment has been extensively commercialized as a food colorant. No. 3600 and E162 are the commercial codes for red beet pigments in U.S.A. and Europe, respectively. Comparison between the 2 kinds of spray-dried pigment powders was undertaken (Table 4). *Amaranthus* powder contained much more betacyanin (0.74% amarantothine) and gave brighter color (higher a\*) than No. 3600 beet powder (0.31% betanin). *Amaranthus* powder had lower H<sup>o</sup> (-4.3°), indicating a slightly purple shade of red. No. 3600 had higher H<sup>o</sup> (2.0°), very similar to red color. Additionally, their storage stability differed appreciably, with *Amaranthus* powder having higher pigment retention (87.9%) than No. 3600 (84.3%) at 32% RH and 25 °C after 16-w storage. This probably resulted from differences in their hygroscopicity. No. 3600 (58.8 g/100 g) absorbed moisture more easily than *Amaranthus* powder (48.5 g/100 g). It was observed that both of them had good solubility. The results of comparison with the commercial beet powder suggested that spray-dried *Amaranthus* pigment powder would be suitable for use as a food-grade colorant.

### Conclusion

HIGHER SPRAY DRYING AIR TEMPERATURES RESULTED IN HIGHER drying rate and higher powder productivity, but over 180 °C/96 °C (inlet/outlet) caused more betacyanin losses, and influenced pigment storage stability. Temperatures of 165 to 180 °C/92 to 96 °C and 20 to 40% feed solid content were suitable for production of *Amaranthus* betacyanin extracts with less pigment degradation. Various carrier and coating agents significant-

ly affected the properties and storage stability of the spray-dried betacyanin powders. Maltodextrins of 25 and 10 DE gave the highest pigment retention (97.3% and 88.7%) at 5% and 32% RH, respectively. There was positive interaction between lower DE and higher DE maltodextrins as combined carrier agents in spray drying. This study demonstrated the feasibility of production of spray-dried *Amaranthus* betacyanin extracts as a foodgrade colorant.

### References

- Anandaraman S, Reineccius GA. 1986. Stability of encapsulated orange peel oil. *Food Technol.* 40 (11): 88-93.
- Anon. 1973. Exotic flavors for cocktail mixes captured with versatile spray drying aid. *Food Prod. Dev.* 7(5): 70-73.
- AOAC. 1990. Moisture in cereal adjuncts: air oven method (103-104°C). *Official Methods of Analysis*, 15<sup>th</sup> ed., Association of Official Analytical Chemists: Arlington, VA.
- Beatus Y, Raziel A, Rosenberg M, Kopelman IJ. 1985. Spray-drying microencapsulation of paprika oleoresin. *Lebensm. Wiss. U. Technol.* 18: 28-34.
- Bhandari BR, Dumoulin ED, Richard HMJ, Noleau I, Lebert AM. 1992. Flavor encapsulation by spray drying: application to citral and linalyl acetate. *J. Food Sci.* 57: 217-221.
- Cai YZ, Corke H. 1999. *Amaranthus* betacyanin pigments applied in model food systems. *J. Food Sci.* 64: 869-873.
- Cai YZ, Sun M, Corke H. 1998a. Colorant properties and stability of *Amaranthus* betacyanin pigments. *J. Agric. Food Chem.* 46: 4491-4495.
- Cai YZ, Sun M, Wu HX, Huang RH, Corke H. 1998b. Characterization and quantification of betacyanin pigments from diverse *Amaranthus* species. *J. Agric. Food Chem.* 46: 2063-2070.
- Desobry SA, Netto FM, Labuza TP. 1997. Comparison of spray-drying, drum-drying and freeze-drying for β-carotene encapsulation and preservation. *J. Food Sci.* 62: 1158-1162.
- Francis FJ. 1986. *Handbook of Food Colorant Patents*. Food & Nutrition Press, Inc., Trumbull, Conn, p. 14-19.
- Francis FJ. 1999. FD&C Colorants: Anthocyanins and Betalains. Pages 33-42, 55-66. In *Colorants*; Francis FJ (Ed.), Eagan Press, St. Paul, Minn.
- Fu WY, Etzel MR. 1995. Spray drying of *Lactococcus lactis* ssp. *Lactis* C2 and cellular injury. *J. Food Sci.* 60: 195-200.
- Glicksman M. 1969. Gum Technology in the Food Industry. In *Food Science & Technology A Series of Monographs*. Academic Press, Inc., New York, NY.
- Hendry GAF, Houghton JD. 1996. *Natural Food Colorants*, Blackie Academic & Professional, London, UK, p. 59-64.
- Huo GH, Guo CZ. 1994. Exploiting study on the red pigment in *Amaranthus tricolor*. *Acta Agric. Univ. Jiangxiensis* (in Chinese) 16: 106-111.
- Jackman RL, Smith JL. 1996. Anthocyanins and betalains. In *Natural Food Colorants*, Hendry GAF, Houghton JD. (Ed.), Blackie Academic & Professional, London, UK, p. 284, 289.
- King AE. 1985. Studies on the production of banana juice powder using spray drying. *J. Chinese Agric. Chem. Soc.* (in Chinese) 23: 62-72.
- Liu HJ, Corke H, Ramsden L. 1999. Physical properties and enzymatic digestibility of phosphorylated *ae. ux* and normal maize starch prepared at different pH levels. *Cereal Chem.* 76: 938-943.
- Main JH, Clydesdale FM, Francis FJ. 1978. Spray drying anthocyanin concentrates for use as food colorants. *J. Food Sci.* 43: 1693-1694, 1697.
- Masters K. 1985. *Spray Drying Handbook*, 4th ed., George Godwin, London, England.
- Pasch JH, von Elbe JH. 1975. Betanine degradation as influenced by water activity. *J. Food Sci.* 40: 1145-1146.
- Piattelli M, Giudici de Nicola M, Castrogiovanni V. 1969. Photocontrol of amarantothine synthesis in *Amaranthus tricolor*. *Phytochemistry* 8: 731-736.
- Piattelli M, Minale L, Prota, G. 1964. Isolation and structure of amarantothine and isoamarantothine. *Ann. Chim.* 54: 963-968.
- Revie GN, Thomas BR Jr. 1972. Powdered flavors offer many advantages. *Food Manuf.* 37(1): 40-41.
- Saguy I, Kopelman IJ, Mizrahi S. 1978. Thermal kinetic degradation of betanin and betalamic acid. *J. Agric. Food Chem.* 26: 360-362.
- Schnetzler KA, Breene WM. 1994. Food uses and amaranth product research: a comprehensive review. In *Amaranth Biology, Chemistry, and Technology*; Paredes-López, O. (Ed.), CRC Press: Boca Raton, FL, p. 155-184.
- von Elbe JH, Maing I-Y, Amundson CH. 1974. Color stability of betanin. *J. Food Sci.* 39: 334-337.
- Wagner LA, Warthesen JJ. 1995. Stability of spray-dried encapsulated carrot carotenes. *J. Food Sci.* 60: 1048-1053.
- MS 19991233

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