ELSEVIER

PII: S0308-8146(97)00235-5

Food Chemistry, Vol. 63, No. 1, pp. 33–37, 1998

Printed in Great Britain
0308-8146/98 $19.00 + 0.00

Chemical stability of encapsulated aspartame in cakes without added sugar

Clinton R. Wetzel* & Leonard N. Bell†

Nutrition and Food Science, Auburn University, AL 36849, USA

(Received 28 May 1997; accepted 5 October 1997)

Encapsulated aspartame (APM), developed to protect the APM molecule during baking, has not been evaluated for stability during baking and subsequent product storage. Thus, the objectives of this project were to determine the APM recovery in various cake formulations after baking and to evaluate APM degradation kinetics during product storage. The recovery of encapsulated APM after baking was 33–34% while that of non-encapsulated APM was 22%. The addition of the acidulant glucono–delta lactone (GDL) to the formulation increased the recovery of encapsulated APM to 58%. The rate constants of APM degradation in the cakes with and without GDL at 22°C were 0.0085 and 0.035 day^{-1}, respectively. By using 2.5% encapsulated APM in cupcake mixes for home preparation, enough APM should remain to provide adequate sweetness during typical product shelf life. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The high-intensity sweetening agent aspartame (N-L-α-aspartyl-L-phenylalanine-1-methyl ester) has been successfully incorporated into numerous foods including breakfast cereals, carbonated and fruit-juice beverages, candy, gelatin, frozen desserts, and dairy beverages for the dietary reduction of sugar and calories (FDA, 1996). Aspartame (APM) is limited to these non-cooking applications due to its instability at elevated temperatures, which yield non-sweet degradation products (Homler, 1984).

While temperature is a major contributor to APM degradation, pH and reactive solutes also influence its stability. The stability of APM is optimal between pH 3 and 5, decreasing under more acidic or basic conditions (Prudel and Davidkova, 1981; Homler, 1984; Ozol, 1986; Tsoubeli and Labuza, 1991; Bell and Labuza, 1991*b*). Buffer salts catalyze the degradation of APM, with greater loss at higher buffer concentrations (Tsoubeli and Labuza, 1991; Bell and Wetzel, 1995). Similarly, at elevated temperatures, APM has been shown to react with reducing sugars via the Maillard reaction (Stamp and Labuza, 1983). In low to intermediate moisture systems, APM degradation increases as water activity increases (Bell and Labuza, 1991*a*; Bell and Hageman, 1994). Overall, APM is most vulnerable when heated for an extended amount of time in high moisture systems at pH values greater than 6, which are the conditions of most baking applications.

To make APM suitable for baking, it must be protected from the simultaneous exposure to ingredients (e.g. water, buffer salts) and environmental stresses (i.e. high temperature) which enhance degradation. An encapsulated form of APM called NutraSweet Custom Encapsulated 20 (NutraSweet Co., Mt Prospect, IL) has been approved for use in baked goods to improve the thermal stability of APM. The encapsulant surrounding APM is hydrogenated cottonseed oil, which comprises 80% of the product, with the remaining 20% being APM (NutraSweet, 1994*a*). The encapsulant isolates APM from the aqueous environment until an internal temperature of 63°C (145°F) is reached (Peck, 1994). At 63°C, the lipid coating melts, resulting in the release of APM, after which it can be perceived as sweet. However, after the release of APM, it is exposed to the environmental stresses which can degrade it. The encapsulant melts near the end of baking to minimize the extent of APM degradation. The maximum amount of encapsulated APM that can be added to the product is 2.5% by weight (or 0.5% pure APM) prior to baking (NutraSweet, 1994*a*). While encapsulated APM contains 8 cal g^{-1}, its low level of usage makes the calorie contribution insignificant (Peck, 1994).

*Currently at Blendco, Inc., Hattiesburg, MS, USA
†To whom correspondence should be addressed at: 328 Spidle Hall, Auburn University, AL 36849, USA. Tel: (334) 844-3272; fax: (334) 844-3268; e-mail: lbell@humsci.auburn.edu

Several technical bulletins discussing the properties and application of encapsulated APM have been written. However, no published research on the stability of encapsulated APM in bakery products exist. Thus, the objectives of this research project were to evaluate the stability of encapsulated APM in various cupcake formulations during baking and storage.

MATERIALS AND METHODS

Cake formulations

Ingredients

The stability of encapsulated APM during baking was evaluated in eight cake formulations, based on the NutraSweet formulation for a no-sugar-added yellow cake (NutraSweet, 1994*b*). Ingredient substitution minimized the number of wet ingredients, creating products which would be representative of a dry cake mix. The basic formulation is summarized in Table 1. The dairy protein used was either a low-lactose whey protein or nonfat dry milk (NFDM). An acidulant, glucono–delta lactone (GDL), was used in four formulations to reduce the final pH of the product, which could enhance the stability of APM upon its release from the encapsulant. One formulation contained oil rather than shortening. In addition, different levels of encapsulated APM (1.25 to 2.0% by weight) were used. Cakes with non-encapsulated APM were also prepared and analyzed to determine how much the encapsulant enhanced APM stability during baking.

Table 1. Overview of cake formulations

Ingredients	%
Encapsulated aspartame (NutraSweet Co., Mt. Prospect, IL)	1.25–2.0
Glucono–delta lactone (Interstate Brands Corp., Columbus, GA)	0 or 0.3
Dairy Protein[a]	3.0 or 5.0
Maltodextrin —Lo-Dex 5 (Cerestar USA, Inc., Hammond, IA)	16.0–17.4
Sorbitol — NEOSORB P60 (Roquette America, Inc., Keokuk, IA)	5.0
Lipid[b]	10.0
Baking Powder (Kraft General Foods, Inc., White Plains, NY)	2.0
Xanthan Gum (Tic Gums, Inc., Belcamp, MD)	0.1
Vanilla Powder (Ingredient Technology Corp., Mahwah, NJ)	0.05
Whole egg powder (Waldbaum Co., Wakefield, NE)	3.0 or 4.0
Cake flour (Reily Foods Co., New Orleans, LA)	21.0
Water	37.05

[a]Low-lactose whey powder—Alacen 866 (New Zealand Milk Products Inc., Santa Rosa, CA), or non-fat dry milk (Kroger, Cincinnati, OH).
[b]Shortening (Procter and Gamble, Cincinnati, OH) or vegetable oil (Procter and Gamble, Cincinnati, OH).

Preparation

Cupcakes were prepared by the creaming method described by Sultan (1990). Maltodextrin, sorbitol, and shortening were blended with a Hobart mixer (model K5-A) for 2 min at speed 4. The other dry ingredients were added to the mix and blended for 2 min at speed 2. Water was added and mixed for 2 min at speed 1. 35 ± 0.1 g of batter were placed into paper baking cups and baked in a preheated oven at 177°C (350°F) for 20 min.

Stability testing

Loss during baking

Baked cakes were frozen at −80°C after cooling for 30 min; these were analyzed for the amount of APM remaining at a later time as described below. Determinations were done minimally in duplicate.

Storage stability

Four cake formulations were used to evaluate the storage stability of APM: a shortening cake with NFDM and no GDL, a shortening cake with NFDM and GDL, a shortening cake with whey and GDL, and an oil cake with whey and GDL. Cakes were stored in air-tight containers at 22°C. At regular time intervals during a week, duplicate cake samples were frozen at −80°C for analysis at a later time. The loss of APM over time was modeled as a pseudo first order reaction as done previously (Prudel and Davidkova, 1981; Bell and Labuza, 1991*a*, 1994; Tsoubeli and Labuza, 1991; Bell and Wetzel, 1995). Rate constants with 95% confidence limits were calculated using computerized least-squares analysis as described by Labuza and Kamman (1983).

Aspartame analysis

Before analysis, the frozen cakes were refrigerated for 1 h and then weighed to estimate the amount of moisture remaining. Each cake was blended for 1 min in a food blender containing enough distilled water to bring the total water level to 1000 ml (taking into account the amount of moisture in the cake). About 50 ml of the blended mixture was poured into a flask, which was covered and shaken overnight at 4°C. The shaken samples were filtered through a 0.2 μm syringe filter. The filtered solution containing the APM was used for analysis. This extraction method was a modification to that of Bell and Labuza (1991*a*) for APM extraction from solid matrices. Spiked samples were prepared by dissolving non-encapsulated APM into a liter solution containing a cake baked without APM and following the extraction procedure above.

APM was analyzed using reverse phase high performance liquid chromatography (Stamp and Labuza, 1989). Separation occurred on a 150 × 4.6 mm NovaPak C-18 column (Millipore, Milford, MA). The mobile

phase consisted of 20% acetonitrile and 80% 5 mM phosphate buffer (v/v); the mobile phase also contained 7 mM sodium heptanesulfonate as an ion-pair reagent and was acidified to pH 3 with H_3PO_4. The flow rate was 1 ml min^{-1} while detection of APM was at 214 nm. Analysis of the spiked samples gave an average recovery of 95.9%, with a coefficient of variation < 1%. Analysis of cakes without APM showed no peak around the APM retention time.

pH and water activity analyses

Cakes with and without GDL were also analyzed for pH after baking. Equal amounts by weight of water and cupcake were stirred in a beaker, forming a slurry. The pH of the mixture was taken with an Orion model 920A pH meter. While this procedure does not yield the true pH of the cupcake (Bell and Labuza, 1992), it does give a value for which to compare between samples. All measurements were performed in duplicate.

Water activity of the cakes was measured with an Aqualab CX-2 (Decagon, Pullman, WA).

RESULTS AND DISCUSSION

Encapsulated APM stability to baking

The APM recovery in cakes ranged from 22–58%, depending upon the formulation (Table 2). In the absence of GDL, the average recovery of encapsulated APM from cakes containing 3% dairy protein was approximately 33–34%, regardless of the type of dairy protein or initial concentration of APM. The amount of lactose from the NFDM was not large enough to promote enhanced APM degradation during baking via the Maillard reaction. Similarly, because the degradation of APM follows pseudo first order kinetics (Prudel and Davidkova, 1981; Bell and Labuza, 1991*a*, 1994; Tsoubeli and Labuza, 1991; Bell and Wetzel, 1995), the percent recovery should be independent of the initial concentration (Alberty, 1987).

Table 2. Average recovery of aspartame (APM) from cakes with standard deviation

Ingredient variation	Recovery (%)
2% Encapsulated APM, 3% NFDM, Shortening ($n=4$)	34.8 ± 0.8
2% Encapsulated APM, 3% Whey, Shortening ($n=2$)	32.9 ± 1.3
1.5% Encapsulated APM, 3% Whey, Shortening ($n=2$)	32.0 ± 1.2
2% Encapsulated APM, 3% NFDM, Shortening, GDL ($n=4$)	57.2 ± 0.7
1.5% Encapsulated APM, 3% Whey, Shortening, GDL ($n=2$)	58.0 ± 2.8
1.25% Encapsulated APM, 3% Whey, Shortening, GDL ($n=6$)	58.6 ± 1.2
1.25% Encapsulated APM, 5% Whey[a], Shortening, GDL ($n=2$)	47.2 ± 0.3
1.25% Encapsulated APM, 5% Whey[a], Oil, GDL ($n=2$)	46.8 ± 1.0
Non-encapsulated APM, 3% NFDM, Shortening ($n=6$)	22.4 ± 0.7
Non-encapsulated APM, 3% NFDM, Shortening, GDL ($n=2$)	34.8 ± 0.2

[a]These cakes also contained 33% more whole egg powder (4% by weight).

The recovery of APM from freshly baked cakes was influenced by the addition of GDL. Cakes containing encapsulated APM, GDL, and 3% dairy protein retained approximately 58% of their initial APM concentration after baking, regardless of the dairy protein type or initial APM concentration. Cakes without GDL had lower APM recoveries (33–34%), as mentioned previously. The pH values of the cake slurries indicated that GDL lowered the final pH of the cake by 0.6–0.8 pH units (from pH 6.8–6.9 to 6.0–6.3 in the slurries). This decreased pH would allow for increased stability of the released APM and consequently a larger APM recovery as compared to cakes without GDL. This type of pH effect on APM stability is similar to that demonstrated previously in solid model systems (Bell and Labuza, 1991*a*,*b*).

The cakes containing a higher protein concentration (5% whey and 4% whole egg powder) and GDL had recoveries intermediate to the other cakes with and without GDL (Table 2). The type of lipid did not influence APM recovery in these cakes. While the pH of these cakes was lowered due to the GDL, the extra whey and egg powder may have contributed salts (e.g. phosphates), which could catalyze the degradation of APM once released from the encapsulant. Phosphate buffer salts have been shown to have a strong catalytic effect on the degradation of APM (Bell and Wetzel, 1995). These counteracting effects of the lowered pH and the possibly higher concentration of residual phosphate would result in the observed intermediate recovery of around 47%.

Another factor which had a large impact on the recovery of APM was the encapsulation. Cakes containing non-encapsulated APM had lower recoveries than comparable cakes containing encapsulated APM (Table 2), indicating that the lipid encapsulant enhanced the stability of APM to baking. By encapsulating APM, the recovery was improved by 50–70% as compared to non-encapsulated APM. However, a NutraSweet technical bulletin lists the recovery as 79% for a yellow cake (NutraSweet, 1994*a*), which is substantially larger than the values obtained in this study. Based on another technical bulletin (NutraSweet, 1994*b*), this cake appears to be prepared as a layer cake rather than small cupcakes. Both cakes were baked at the same temperature, but the cupcakes, being smaller, were baked for 10 min less than the layer cake. Despite the shorter bake time of the cupcakes, their smaller size may have allowed for enhanced heat transfer, resulting in a higher internal cake temperature than that of the layer cake

and consequently a greater extent of APM degradation. Thus, to optimize the recovery of encapsulated APM after baking, the formulation pH, ingredient type, geometry of the pans, and the baking time and temperature should all be taken into account.

Storage stability of aspartame

Figure 1 shows the pseudo first order plot for APM degradation during storage at 22°C in cakes containing 2% encapsulated APM, 3% NFDM, and shortening with and without GDL. These cakes had a water activity (a_W) of 0.93 and a pH of approximately 6.8–6.9 (no GDL) or 6.0–6.3 (with GDL). The higher initial APM concentration in the GDL cakes is indicative of the greater APM recovery due to the lower pH as mentioned previously. If no APM was lost during baking, the APM concentration in these cakes would initially have been 5 mg APM g^{-1} cake.

The rate constant for APM degradation with 95% confidence limits was determined to be $0.035 \pm 0.005\ d^{-1}$ for the cake without GDL (pH ≈ 6.8). This rate constant translates into an APM half-life of 19.8 days. Thus, cupcakes stored for 3 days would lose approximately 10% of the remaining APM. If the maximum allowable amount of encapsulated APM (i.e. 2.5%) was formulated into the cakes, the product would reach a sweetness level similar to full-sugar cakes in 6–8 days, assuming the sweetness of APM is 180–200 that of sucrose (Homler, 1984). This time would be an adequate shelf life for cupcakes prepared from mixes at home, which are consumed within 3–4 days, but not for prepackaged baked cakes which require longer shelf lives.

The rate constant for APM degradation in the cake with GDL was $0.0085 \pm 0.0063\ day^{-1}$ which yields a half-life of 81 days. Theoretically, for an acid/base catalyzed reaction in the absence of buffer salts, the reaction rate constant would decrease by a factor of 10 for each

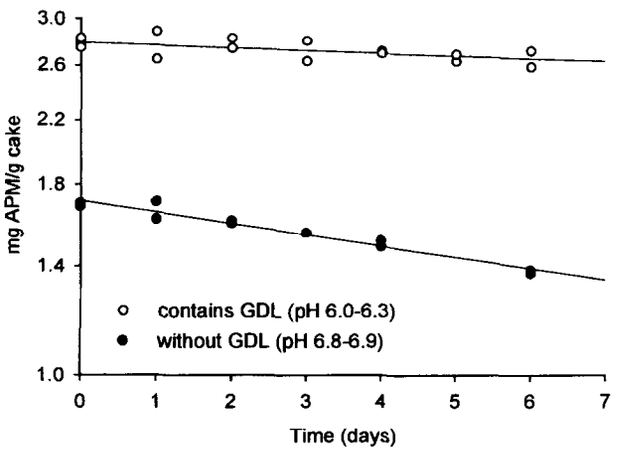

Fig. 1. Pseudo first order plot for the degradation of encapsulated aspartame in cupcakes containing shortening, 3% NFDM, and 3% egg powder with and without glucono–delta lactone (a_W 0.93) during storage at 22°C.

pH unit drop (Alberty, 1987; Bell and Labuza, 1991*b*). In practice, it has been shown that between pH 7 and 5, the APM stability increases between 8 and 16 times for each unit decrease in pH (Prudel and Davidkova, 1981; Homler, 1984; Bell and Labuza, 1991*b*, 1994). Assuming pH values of 6.2 and 6.8 for the cakes with and without GDL, respectively, a one unit decrease in pH would increase the stability by a factor of 10.6, which is consistent with previous data as well as that theoretically expected. Making the same assumptions as the previous cake, this cake would reach the sweetness level of a full-sugar cake in 90 days, which would be suitable for prepackaged products. However, the effect of GDL and the lower pH on the textural and sensory properties of the cake need to be evaluated.

In this study, the APM half-lives in the pH 6–7 range at a_W 0.92 and 22°C were larger than expected based on previously published data from other high a_W systems. Prudel and Davidkova (1981) determined the APM half-life was 0.5 days in solution at pH 6.95 and 20°C. Using data from Bell and Labuza (1991*a*), APM in 0.1 M phosphate buffer at pH 7 and 20°C had a half-life of less than 0.5 days. Similarly, using the 1.3 day half-life of APM in a dairy beverage at pH 6.7 and 30°C (Bell and Labuza, 1994) and extrapolating to 20°C using a Q_{10} value of 2.3 for APM degradation in solution at pH 7 (Bell and Labuza, 1991*a*), the dairy beverage would have an APM half-life of approximately 3 days. In addition, APM in 0.01 M phosphate buffer and citrate buffer solutions at pH 7 and 25°C had half-lives of 2.0 and 5.3 days, respectively (Bell and Wetzel, 1995). One major difference between our cake system and the experimental systems of previous studies is the presence of buffer salts. Bell and Wetzel (1995) demonstrated that catalysis by buffer salts add a significant contribution to the overall APM degradation rate constant. The only buffer salts in the cake are those found naturally at low levels in the ingredients. Thus, while the lower water activity would increase the APM stability to some extent as compared to in solution, the very low buffer salt concentration is believed to be the major reason the APM stability in the cake was greater than that found in previous solution studies.

Figure 2 shows a plot of APM degradation in cakes containing GDL and extra whey and egg powder. As seen in this plot, little difference in the data was observed by replacing the shortening with oil. This result is consistent with the data of Kamman and Labuza (1985), which showed glucose loss from the Maillard reaction was not influenced by the type of lipid (i.e. shortening or oil) at a water activity of 0.81. The rate constant for the loss of APM in cakes containing GDL and extra protein was $0.030 \pm 0.007\ day^{-1}$ (i.e. a half-life of 23.1 days), which was not significantly different from the loss of APM from cakes containing less protein without GDL. While the lower pH of these cakes would enhance the stability of APM as compared to the cake without GDL, the extra protein (whey and

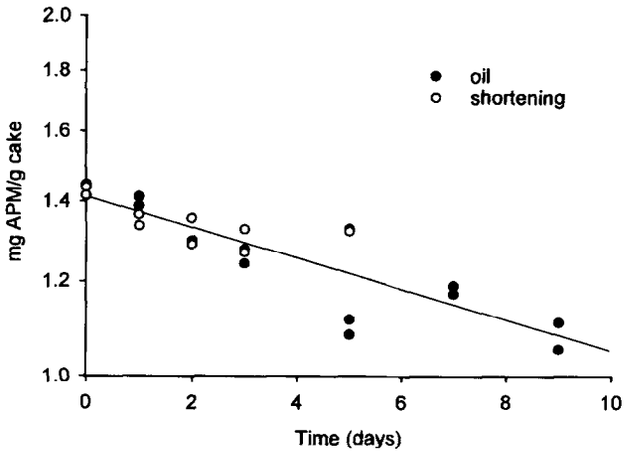

Fig. 2. Pseudo first order plot for the degradation of encapsulated aspartame in cupcakes containing 5% whey, 4% egg powder, and glucono–delta lactone (a_W 0.93, pH 6.0–6.3) during storage at 22°C.

whole egg powder) could contribute additional salts which catalyze the degradation of APM as discussed previously. The stabilizing effect of the lower pH and the destabilizing effect of greater residual salts counteract each other, resulting in a degradation rate similar to cakes without GDL.

The rates of APM degradation in various cake formulations suggest that, depending upon ingredients and the initial APM concentration, sufficient APM should remain during typical storage times to sweeten the cakes.

ACKNOWLEDGEMENTS

This project was supported by an Auburn University Graduate School Grant-in-Aid. The authors are appreciative to Interstate Brands Corporation, New Zealand Milk Products, Inc., Cerestar USA, Inc., Roquette America, Inc., Tic Gums, Inc., Ingredient Technology Corporation, and Waldbaum Company for donating ingredients to the project.

REFERENCES

Alberty, R. A. (1987) *Physical Chemistry*, 7th ed. John Wiley and Sons, New York.

Bell, L. N. and Hageman, M. J. (1994) Differentiating between the effects of water activity and glass transition dependent mobility on a solid state chemical reaction: aspartame degradation. *Journal of Agricultural and Food Chemistry* **42**, 2398–2401.

Bell, L. N. and Labuza, T. P. (1991*a*) Aspartame degradation kinetics as affected by pH in intermediate and low moisture food systems. *Journal of Food Science* **56**, 17–20.

Bell, L. N. and Labuza, T. P. (1991*b*) Potential pH implications in the freeze-dried state. *Cryo-Letters* **12**, 235–244.

Bell, L. N. and Labuza, T. P. (1992) Evaluation and comparison of simple methods for pH measurement of reduced-moisture solid systems. *Journal of Food Processing and Preservation* **16**, 289–297.

Bell, L. N. and Labuza, T. P. (1994) Aspartame stability in commercially sterilized flavored dairy beverages. *Journal of Dairy Science* **77**, 34–38.

Bell, L. N. and Wetzel, C. R. (1995) Aspartame degradation in solution as impacted by buffer type and concentration. *Journal of Agricultural and Food Chemistry* **43**, 2608–2612.

FDA (1996) *Code of Federal Regulations*. 21/P. 172.804. Office of the Federal Register, Washington, DC.

Homler, B. (1984) Properties and stability of aspartame. *Food Technology* **38**(7), 50–55.

Kamman, J. F. and Labuza, T. P. (1985) A comparison of the effect of oil vs shortening on the rates of glucose utilization in non-enzymatic browning. *Journal of Food Processing and Preservation* **9**, 217–222.

Labuza, T. P. and Kamman, J. F. (1983) Reaction kinetics and accelerated tests simulation as a function of temperature. In *Computer-Aided Techniques in Food Technology*, ed. I. Saguy, pp. 71–115, Marcel Dekker, Inc., New York.

NutraSweet (1994*a*) Baked goods: technical overview. Bulletin #5323. NutraSweet Co., Deerfield, IL.

NutraSweet (1994*b*) Baked goods: formulations. Bulletin #5704. NutraSweet Co., Deerfield, IL.

Ozol, T. (1986) Stability of aspartame in artificial syrups. *Acta Pharmaceutica Turcica* **28**, 125–130.

Peck, A. (1994) Intense sweeteners for bakery products. *American Institute of Baking Technology Bulletin* **16**(2), 1–8.

Prudel, M. and Davidkova, E. (1981) Stability of L-aspartyl-L-phenylalanine methyl ester hydrochloride in aqueous solutions. *Die Nahrung* **25**(2), 193–199.

Pyler, E. J. (1988) *Baking Science and Technology*. 3rd ed. Sosland Publishing Company, Merriam, KS.

Stamp, J. A. and Labuza, T. P. (1983) Kinetics of the Maillard reaction between aspartame and glucose in solution at high temperatures. *Journal of Food Science* **48**, 543–547.

Stamp, J. A. and Labuza, T. P. (1989) An ion-pair high performance liquid chromatographic method for the determination of aspartame and its decomposition products. *Journal of Food Science* **54**, 1043–1046.

Sultan, W. J. (1990) *Practical Baking*. 5th ed. Van Nostrand Reinhold, New York.

Tsoubeli, M. and Labuza, T. P. (1991) Accelerated kinetic study of aspartame degradation in the neutral pH range. *Journal of Food Science* **56**, 1671.