J. Agric. Food Chem. **2004,** *52,* 2623–2627 **2623**

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Flavor Release and Perception in Hard Candy: Influence of Flavor Compound–Compound Interactions

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The influence of flavor compound−compound interactions on flavor release properties and flavor perception in hard candy was investigated. Hard candies made with two different modes of binary flavor delivery, (1) L-menthol and 1,8-cineole added as a mixture and (2) L-menthol and 1,8-cineole added separate from one another, were analyzed via breath analysis and sensory time−intensity testing. Single-flavor candy containing only L-menthol or 1,8-cineole was also investigated via breath analysis for comparison. The release rates of both L-menthol and 1,8-cineole in the breath were more rapid and at a higher concentration when the compounds were added to hard candy separate from one another in comparison to their addition as a mixture (conventional protocol). Additionally, the time−intensity study indicated a significantly increased flavor intensity (measured as overall cooling) for hard candy made with separate addition of these flavor compounds. In conclusion, the flavor properties of hard candy can be controlled, at least in part, by flavor compound−compound interactions and may be altered by the method of flavor delivery.

KEYWORDS: Flavor release; perception; hard candy; flavor compound−compound interactions; L-menthol; 1,8-cineole; eucalyptus

INTRODUCTION

Flavor−matrix interactions in food products have been widely investigated with respect to influences on flavor release and flavor perception. Defining key matrix parameters that influence the release of flavor compounds from foods would provide useful information to tailor (control) the flavor response of food products and allow for the effective use of flavor materials. Traditionally, researchers have focused on how different food constituents (i.e., protein, carbohydrate, fat, salt) or the food structure (i.e., emulsions, viscosity) affects flavor release (*1*−*3*).

Whereas previous studies on flavor−matrix interactions have primarily focused on food macromolecules, in specific food products, such as hard candy, interactions among the flavor compounds themselves may likewise influence their release and subsequent perception. The nonsweetener flavor component of hard candy exists in pocket-like cavities (dispersion) and is extremely limited in mobility due to the sugar glass matrix. As a result, interactions among the compartmentalized flavor compounds in hard candy are facilitated. Furthermore, hard candy is not only a unique food system because of its basic composition of simple sugars and maltodextrins, but it also has a relatively high abundance of flavor (volatile and nonvolatile) compounds.

Previous work by Hills and Harrison (*4*) took advantage of the simplistic composition of hard candy and used it as a model food system to investigate flavor release theories. The basic characteristics of hard candy allowed them to make several mathematical assumptions while offering a real food system for in vitro and in vivo investigation. On the basis of the direct measurement of dye from hard candy during dissolution (via spectrophotometer), they showed that two-layer stagnant film theory best describes the mechanism of flavor release from hard candy. However, their study did not address the influence of possible flavor compound−compound interactions on subsequent release kinetics.

More recently, the impact of the nonvolatile flavor fraction on the sensory perception of mint and strawberry flavors was reported to have a critical role in the perceived flavor intensity (*5*). In both studies sucrose, for example, was determined to largely influence flavor perception. Davidson et al. (*6*) reported that the decrease in chewing gum mint flavor intensity was highly correlated to the decrease in sucrose concentration released from the gum matrix over time. Likewise, Cook et al. (*5*) showed that the removal of sucrose from a liquid strawberry flavor system resulted in little or no perception of fruit flavor. Although other parameters were also examined, it was clear that the nonvolatile sweetener fraction (sucrose) had the greatest influence on the perceived strawberry flavor intensity.

The delivery of flavor compounds from hard candy to the saliva for subsequent release/perception is a function of the product dissolution, and therefore the ratio of nonvolatile to volatile compounds remains constant throughout the consumption period. Consequently, hard candy can serve as a model to

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10.1021/jf0353133 CCC: $27.50
Published on Web 04/06/2004

Table 1. Hard Candy Model Formulation

ingredients for cooking	amount (g)
corn syrup (42DE)	308.2
sucrose	302.5
water	55
flavor premix[a]	15[b]

[a] Added after cooking. [b] Does not account for the weight of the flavor compounds.

characterize the influence of flavor−matrix interactions on the flavor release properties and subsequently flavor perceptions that are not related to a change in the ratio of sugar (sweetener) to the other flavor compounds present.

The objectives of this study were to determine whether flavor compound−compound interactions influence the volatile flavor release kinetics and the flavor perception in hard candy.

MATERIALS AND METHODS

Materials included L-menthol (Sigma Aldrich, Milwaukee WI), eucalyptus oil (analytically measured as 1,8-cineole) (International Flavors and Fragrances, Hazlet, NJ), sugar (Jack Frost, Refined Sugar Inc., Yonkers, NY), 42 DE corn syrup (Cargill, Minneapolis MN), hexane (Baxter Burdick & Jackson, Muskegon MI, >99% purity), and 1-octanal (Aldrich Chemical, Milwaukee WI, 99% purity.)

Sample Preparation. Hard candy was prepared in laboratory scale batches, which yielded ∼500 g of finished candy. Four different treatments of hard candy using two volatile flavor compounds, l-menthol and/or 1,8-cineole (as eucalyptus oil), were made. The target quantities of each compound remained constant for all treatments at 7 mg for L-menthol and 3 mg for 1,8-cineole per 4 g (drop) of candy. The details of the four treatments are as follows: (1) L-menthol and 1,8-cineole added together (as a mixture) to the candy; (2) L-menthol added alone to the candy; (3) 1,8-cineole added alone to the candy; and (4) L-menthol and 1,8-cineole added separately to the candy.

The hard candy was prepared by mixing all of the ingredients except the flavor premix (see **Table 1**) in a 2-qt stainless steel pot and heated under gentle continual stirring until a temperature of 110 °C was reached. The sugar mixture was then heated, without stirring, to 130 °C, after which it was stirred constantly to a temperature of 133 °C. The mixture then finished cooking, undisturbed, until it reached 145 °C. Immediately after cooking, 483 ±1 g of the sugar mixture was quickly poured out onto a marble slab, and the flavor compounds in the form of a flavor premix (detailed below) were added.

The flavor premix was added in a line onto the center of the hot sugar glass material, which was immediately folded onto itself to cover and melt the premix and then folded twice more to fully entrap the flavor compounds and create the candy material. At this point the candy was picked up with gloved hands and repeatedly folded for equal distribution of flavor. After ∼25 folds, the flavor compounds were completely incorporated into the candy and the mass had cooled enough to be molded into oval drops using a drop roller (model 93STM, Nuova Euromec). To facilitate molding, the candy mass was cut into two or three portions, and then each was put through the drop roller. Typically, a batch of candy yielded 20−30 candies suitable for analysis (no visible defects).

The flavor premix consisted of the flavor compounds (in liquid form) mixed into 15 g of a powdered sugar glass matrix. This material was created by making the hard candy sugar matrix (see **Table 1**) as described above (without postcooking flavor addition) and subsequently grinding it into a powder using a laboratory blender (Waring, Tarrington, CT).

In general, the procedure for making the four candy treatments was unchanged from that described above; the only alterations made were in regard to how the flavor compounds were introduced into the candy. For treatments 1−3 the flavor compounds were added to the powdered candy as a single premix (15 g). In the case of treatment 4 the aroma premix was divided into two equal parts (one for each flavor compound). One part contained 1,8-cineole in 7.5 g of powdered candy, whereas the other consisted of L-menthol in 7.5 g of powdered candy. These two premixes were then incorporated into the candy by first adding the 1,8-cineole premix, folding once, adding the L-menthol premix, folding again, and then proceeding as described previously to distribute flavor and mold the candy into drops.

The amount of L-menthol and 1,8-cineole added to the premix for all four treatments ranged from 1.4 to 1.7 g/500 g of finished candy for L-menthol and from 0.5 to 0.7 g/500 g of finished candy for 1,8-cineole as necessary to achieve final concentrations of 1.75 mg for L-menthol and 0.75 mg for 1,8-cineole per gram of candy. Variation in the amounts of flavor used was a result of uncontrollable losses due to heat; therefore, addition of excess flavor was necessary. All treatments were reformulated until quantification indicated the desired quantity of L-menthol and 1,8-cineole, within ±5% (means) and a standard deviation within 10%, were obtained.

Quantification of Volatile Flavor Compounds in Hard Candy. Six candies from each treatment were randomly selected for subsequent quantification of L-menthol and 1,8-cineole. The selected candies were split in half and weighed into 20-mL clear glass sample vials (I-Chem, New Castle, DE). Seven grams of distilled water was then added to each vial, and the vials were with closed with Teflon screw caps and placed in a water bath at 38 °C for 1 h to completely dissolve the candy. At 15-min intervals the vials were removed from the bath, lightly shaken for 10 s, and returned. After an hour at 38 °C, the vials were left to cool at room temperature for 20 min. Once at room temperature, 5 mL of a hexane containing 1-octanal (2.04 mL/L) as an internal standard was added to each vial. The vials were shaken vigorously in turn for 10 s until each vial had been shaken four times and then allowed to sit at room temperature for 45 min (to ensure complete separation of water and hexane). An aliquot of the solvent layer was then removed and analyzed via an Agilent 6890 gas chromatograph (Wilmington, DE) utilizing a flame ionization detector equipped with a Combi-Pal autosampler (CTC Analytics, Zwingen, Switzerland) and a DB-5 capillary column (Agilent Technologies, Palo Alto, CA) with the following dimensions: 30 m × 0.25 mm with a 0.25-μm film thickness. The gas chromatography operating conditions were as follows: 1 μL of sample was injected in split mode (50:1); inlet temperature was 200 °C, detector was 250 °C, oven program was 40 °C for 2 min, then increased at 10 °C/min to 140 °C, then increased at 35 °C/min to 250 °C, and held for 2 min; constant flow rate of 1.2 mL/min (H_2). Flavor concentrations were determined from peak areas in reference to a standard curve (measured in duplicate), which consisted of L-menthol and 1,8-cineole spiked into a model matrix (4 g of candy sugar mixture in 7 g of distilled water) at five levels (2.10, 4.55, 7.00, 9.45, and 11.90 μg and 0.90, 1.95, 3.00, 4.05, and 5.10 μg/4 g of candy model, respectively, $r^2 = 0.99$) and following the extraction/analytical procedure outlined above.

Breath Analysis. A modified Quattro II/Micromass mass spectrometer (Waters, Milford, MA) for direct/continuous sampling of the breath from the nose was used to monitor release of volatile flavor compounds from hard candy *in vivo*. Two subjects were used for breath analysis, and each subject performed three replications for each candy treatment (number of panelists used was restricted due to the limited amount of benchtop candy produced with the required flavor quantities). The subjects were instructed to place a candy onto their tongues, close their mouths, and align themselves (nose) with the breath analysis instrument inlet before beginning to swirl and suck the candy without chewing. Each candy was sucked for 4 min. All candies were of similar weight and shape. To eliminate carry-over, each subject waited at least 20 min between samples and rinsed repeatedly with water. In addition, before each sample, the subjects were instructed to breathe into the breath analysis instrument to verify that baseline levels, for the flavor compounds being monitored, had been reached. All analyses were performed over a two day period such that two treatments were performed each day. The breath analysis instrument operating conditions were as follows: APCI mode, "nosespace" sampling rate was 100 mL/min; block temperature was 120 °C; transfer line was 100 °C; corona discharge was 4 kV; cone voltage was 20 V; drying gas was 6.7 L/min; sheath gas was 3.8 L/min. Ions monitored were 139 $[M + H - H_2O]^+$ for L-menthol and 156 $[M + H + 1]^+$ for cineole at a sampling rate of

8 Hz. The carbon-12 ion of cineole was not monitored due to instances of maximized detector signal during the analysis, and therefore the carbon-13 ion was monitored to extend the analytical range of measurement. Quantification of L-menthol and 1,8-cineole directly from the breath was determined via standard curve (in duplicate). Five different levels of each compound (0.0056, 0.0448, 0.2856, 1.3200, and 6.6000 μg for L-menthol and 0.0048, 0.0384, 0.2448, 1.3800, and 6.6000 μg for 1,8-cineole) dissolved in pentane were injected (both compounds at the same time) into a specialized airtight water-jacketed 1.1-L deactivated glass vessel, which was maintained at 40 °C and held for 5 min with constant stirring prior to interfacing directly to the breath analysis instrument using the same operating conditions at described above. The peak height (ion intensity) versus mass of compound per liter air was plotted ($r^2 = 0.99$).

Sensory Analysis. The time−intensity (TI) sensory study was performed using a trained panel of five judges (three females and two males), ages 24−40 years. The panelists were selected on the basis of prior experience in sensory evaluations and availability.

Training was done in two phases. The first phase consisted of seven practice sessions, which allowed the panel to become familiar with the flavor characteristics of the laboratory-made l-menthol/1,8-cineole candy, as well as to become familiar with the time−intensity evaluations and the software program (Compusensefive v 4.2, Guelph, ON, Canada). This was followed by the second phase (consisting of eight sessions) in which the panelists were instructed to focus on and scale only the intensity of the cooling sensation felt in the mouth and nose during the initial four minutes of sucking on a candy. All practice and evaluation sessions consisted of the continual assessment of one candy for 4 min, making sure the panelists breathed regularly through their noses with their mouths closed while rating the intensity of the overall cooling sensation. The TI data were collected automatically every 0.5 s.

A 15-point scale was used for intensity measurement, with 0 corresponding to no intensity and 15 corresponding to painful intensity. The panelists were given three high-concentration salt solutions as cross-modality references to aid in scaling the intensity of the cooling. A 0.7% salt solution was scaled a 4, with a 6 being a 1.1% solution, and a 1.5% solution at the level of a 9 on the intensity scale.

Evaluation of the candy treatments in duplicate took place over a two-day period with two sessions held each day (with 4 h between same-day sessions) in randomized order. The same batches of candy were evaluated by both breath analysis and sensory evaluations.

RESULTS AND DISCUSSION

The breath analysis release profiles of L-menthol and 1,8-cineole from hard candy with two different modes of flavor delivery (added as a mixture or added separately) are shown in **Figures 1** and **2**. The average variation for each subject was reported to be ±20 ng/L of air for menthol and ±63 ng/L of air for cineole (95% confidence interval; data not shown). Dramatic differences were observed in the volatile flavor release profiles between these two flavor delivery systems. When L-menthol was incorporated separately from 1,8-cineole, the release rate and concentration of L-menthol in the "nosespace" were ~2-fold higher in comparison to those of candy to which the flavor compounds had been added as a mixture (see **Figure 1**). Similarly, the release of 1,8-cineole also increased (rate and concentration) when the flavor compounds were incorporated separately as opposed to as a mixture (see **Figure 2**). Therefore, the release kinetics of volatile flavor compounds from hard candy was affected by the mode of flavor delivery (added as mixture or singularly).

The observed differences in the volatile flavor release properties between the two candy treatments may be explained by flavor compound−compound interactions between L-menthol and 1,8-cineole. The flavor compounds in hard candy exist in pocket-like cavities (dispersion) within the hard candy matrix (glass). When hard candy is consumed (dissolved), the flavor

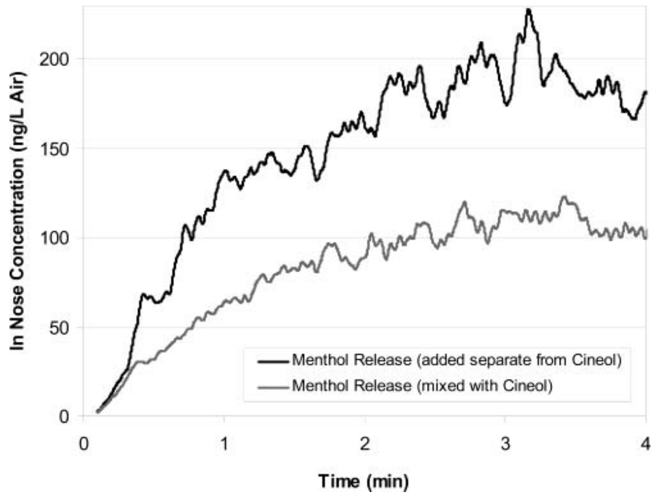

Figure 1. Breath analysis release profile of L-menthol from hard candy comparing two methods of binary flavor delivery to the candy (mixture or separate addition) at equal concentrations. Each curve represents the mean of six replicates (triplicate measurements from two panelists) subsequently smoothed by a 6-s moving average trendline.

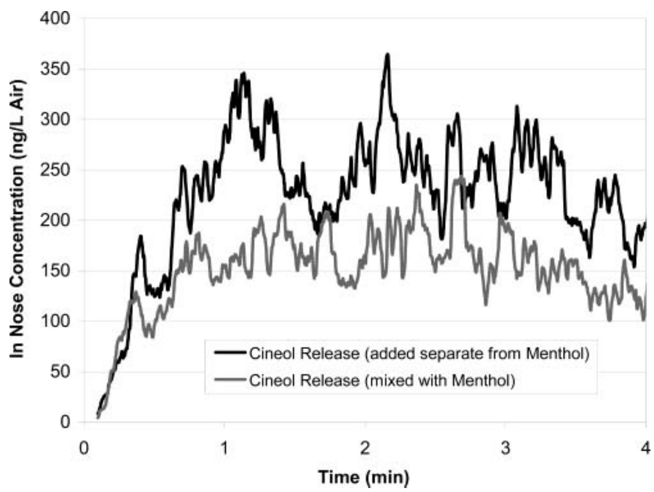

Figure 2. Breath analysis release profile of 1,8-cineole from hard candy comparing the two methods of binary flavor delivery to the candy (mixture or separate addition) at equal concentrations. Each curve represents the mean of six replicates (triplicate measurements from two panelists) subsequently smoothed by a 6-s moving average trendline.

compounds are released as a concentrated material. As a result, when the flavor compounds are added to the candy as a mixture (conventional method), interactions among the compounds can influence their volatile release rates in the mouth. These interactions can further be illustrated by comparing the breath analysis release rate of L-menthol or 1,8-cineole (see **Figures 3** and **4**) when added to hard candy (only one flavor compound added) versus when L-menthol and 1,8-cineole (binary flavor system) were added individually. The release rates of both L-menthol and 1,8-cineole were very similar for these two flavor delivery systems (each was higher in comparison to mixture addition) and indicated that flavor compound−compound interactions can be viewed as an important factor for the control of volatile flavor release in hard candy.

Changes in compound solubility as a result of possible interactions between L-menthol and 1,8-cineole may explain, in part, the noted differences in volatility/release of these compounds during hard candy consumption based on the mode of flavor delivery. L-Menthol is more hydrophilic than 1,8-cineole (as eucalyptus oil), and therefore interactions between

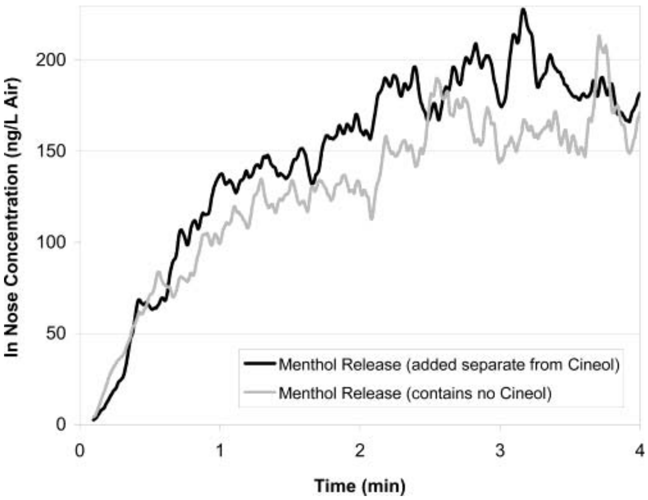

Figure 3. Breath analysis release profile of L-menthol from hard candy containing a single flavor in comparison to that of a binary-flavored candy made via separate flavor addition at equal concentrations. Each curve represents the mean of six replicates (triplicate measurements from two panelists) subsequently smoothed by a 6-s moving average trendline.

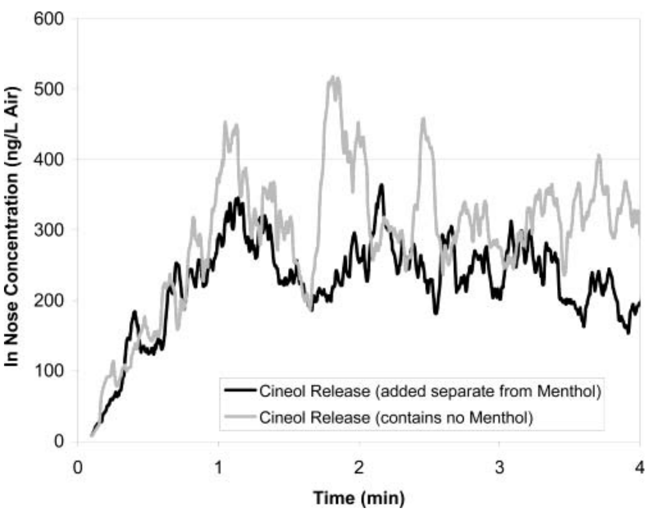

Figure 4. Breath analysis release profile of 1,8-cineole from hard candy containing a single flavor in comparison to that of a binary-flavored candy made via separate flavor addition at equal concentrations. Each curve represents the mean of six replicates (triplicate measurements from two panelists) subsequently smoothed by a 6-s moving average trendline

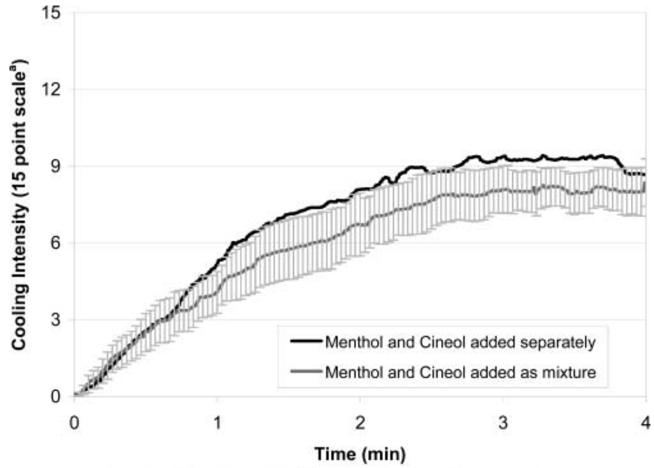

Figure 5. Comparison of perceived cooling intensity from hard candy with different flavor delivery methods over a 4-min evaluation period. Each curve represents the average of five panelists (95% confidence interval is displayed for menthol and cineole added as mixture treatment).

the two compounds could enhance the solubility of 1,8-cineole in an aqueous environment (i.e., saliva in mouth). In contrast, when the flavor compounds were added by separate addition, fewer molecular interactions would be anticipated during consumption (kinetic control). The influence of possible compound interactions on solubility may be illustrated by the following example. A hydrophobic compound when added directly to a 5% ethanol aqueous solution is not soluble; however, if this compound is first added to a 50% ethanol aqueous solution and then slowly diluted to a 5% ethanol concentration, the compound remains in solution. The increased interactions with ethanol at higher concentrations may facilitate formation of colloid structures and alter the thermodynamic properties of the solution. This type of molecular interaction would be expected to reduce the volatility (release) of both compounds.

The mode of flavor delivery utilized may also result in a change of the physical state of the added flavor compounds. For example, L-menthol when mixed with 1,8-cineole is a liquid, but when added separate from 1,8-cineole, it is a solid at 38 °C (mouth temperature). The melting point of L-menthol is 43 °C and therefore would require an additional transition from solid to liquid before it can be dissolved into the saliva during consumption. This additional phase transition might be expected to result in a reduction in the compound volatility during consumption. However, breath analysis indicated a more rapid release of L-menthol when added separately from 1,8-cineole (exists as a solid) in comparison to mixture addition (exists as a liquid). As a result, the additional phase transition was found not to be as influential on the flavor release properties as other flavor compound–compound interactions.

The results of the time–intensity study are shown in **Figure 5**. The overall cooling intensity of the binary flavor treatments, using each method of flavor delivery (mixture and separate addition), were investigated. Overall, the panel indicated that the cooling intensities of the two candy treatments were significantly different after the first minute of consumption (see **Figure 5**, 95% confidence interval). The candy made by separate addition of the two flavor compounds was perceived as having a more intense cooling characteristic. The intensity of the overall cooling sensation was selected for sensory evaluation as it was the most notable flavor response to the sensory panel. L-Menthol has a slight mint aroma but is primarily associated with a cooling (trigeminal) flavor response, whereas 1,8-cineole has a camphoraceous aroma (*7*). Because L-menthol has a trigeminal cooling response, perception occurs even without volatilization. Therefore, part of the cooling sensation can be attributed to nonvolatile L-menthol; however, this is true for all candy treatments. The perceived increase in cooling intensity reported for the separate addition candy treatment correlated with the observed increase in the volatile L-menthol release rate reported from breath analysis. The magnitude of the observed increase for L-menthol from the breath was not directly proportional to the increased sensory response, which would be anticipated for several reasons. First, Stevens's law (*8*, *9*) indicates an exponential relationship between concentration of stimulus and sensation perceived. Second, the flavor concentration was relatively high in the hard candy, and therefore it is likely the sensory response may be in the upper portion of the sigmoid curve relationship between flavor concentration and perceived intensity. Third, the perceived cooling intensity would also be influenced by L-menthol in the saliva, which had not been volatilized. In conclusion, the influence of flavor compound–compound interactions on the flavor properties in hard candy offers new information for the control and effective use of flavor materials in similar products.

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Received for review November 8, 2003. Revised manuscript received February 24, 2004. Accepted February 29, 2004.

JF0353133