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

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The release kinetics of L-menthol dissolved in propylene glycol (PG), Miglyol, or 1,8-cineole (two common odorless flavor solvents differing in polarity and a hydrophobic flavor compound) were monitored from a model aqueous system via atmospheric pressure chemical ionization mass spectrometry (APCI-MS). Breath analysis was also conducted via APCI-MS to monitor release of L-menthol from hard candy that used PG and Miglyol for L-menthol incorporation. The quantities of L-menthol released when dissolved in PG or Miglyol from the model aqueous system were found to be similar and overall significantly greater in comparison to when dissolved in 1,8-cineole. Analogous results were reported by the breath analysis of hard candy. The release kinetics of L-menthol from PG or Miglyol versus from 1,8-cineole were notably more rapid and higher in quantity. Results from the sensory time–intensity study also indicated that there was no perceived difference in the overall cooling intensity between the two flavor solvent delivery systems (PG and Miglyol).

INTRODUCTION

The influence of volatile flavor and nonvolatile food compound interactions on overall flavor release and perception has been widely investigated [see McGorrin and Leland (*1*), Taylor (*2*), and Roberts and Taylor (*3*) for an extensive overview]. Recently, interactions among the volatile flavor compounds themselves have been reported to affect the flavor release kinetics and flavor perception in specific food products (i.e., hard candy) in which the flavor compounds are localized in concentrated packets (*4*). The flavor component of hard candy is entrapped within tiny cavities throughout the sugar glass matrix. As a result, the flavor compounds in hard candy are exceedingly limited in mobility and, therefore, present in a microenvironment that would facilitate any potential flavor compound–compound interactions. Defining the modes of flavor interactions, as well as determining how these interactions influence flavor release kinetics, would provide improved control over flavor delivery in similar food products.

Food manufacturers, including those in the confectionery industry, commonly use flavor compounds that have been dissolved in a "flavor solvent" as a flavoring material (*5*). Consequently, the flavor properties of hard candy may be controlled, in part, by the selection of flavor solvent and the resultant flavor compound–solvent interactions. Flavor solvents function as dispersing agents to facilitate flavor incorporation into food products. The properties of the food product or flavor compound(s) or even the processing conditions can influence the solvent used. For example, an oil soluble flavor solvent would usually be chosen for use in an oil rich food product, whereas in a food in which water is predominant, a water soluble solvent is needed. The matrix properties of hard candy permit the use of a wide range of solvents with varied physicochemical properties, although, due to the high processing temperatures involved in the manufacturing process, high boiling point solvents are normally used.

The flavor component of hard candy would not be anticipated to be released directly from the solvent system but rather be transported into aqueous phase (i.e., saliva) and then into the air phase within the oral cavity for perception (*2*). The amount of solvent in relation to aqueous phase would be infinitesimal, and, as a result, the solvent hydrophobicity would not be expected to be a key factor in the flavor release properties based on Henry's law. The type and extent of flavor interactions in hard candy, however, would ultimately depend on the physicochemical properties of both the flavor compounds and the solvent systems. Previously, Schober and Peterson (*4*) suggested colloidal interaction may possibly influence flavor release in binary-flavored hard candy.

The objectives of this study were to determine whether the release kinetics and cooling perception of L-menthol from hard candy were influenced by the use of two commercially available flavor solvents of different polarities [propylene glycol (PG; hydrophilic) and Miglyol (medium-chain triglyceride; hydrophobic)]. Additionally, 1,8-cineole (as eucalyptus oil; hydrophobic) was also included as a flavor solvent for comparison

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based on the results from a previous study indicating that 1,8-cineole (as eucalyptus oil) when mixed with L-menthol in hard candy influenced the release kinetics of L-menthol (*4*). Although cineole is a flavor compound, it can also serve as a solvent (mp = 1 °C) in that it has the ability to dissolve menthol (mp = 43 °C) and function as a dispersing agent.

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), sucrose (Jack Frost, Refined Sugar Inc., Yonkers, NY), 42 DE corn syrup (Cargill, Minneapolis, MN), propylene glycol (Quest International, Owings Mills, MD), Miglyol 812 (Condea Vista Co., Cranford, NJ), hexane (Baxter Burdick & Jackson, Muskegon MI, >99% purity), tricaprylin (Sigma Aldrich, St. Louis MO, ≥99%), and 1-octanal (Aldrich Chemical, Milwaukee WI, 99% purity).

Sample Preparation. One part to one part solutions of menthol/cineole, menthol/PG, and menthol/Miglyol were prepared for the model aqueous system analysis.

Two different flavor treatments of hard candy were prepared in small laboratory scale batches for breath analysis. Both flavor treatments consisted of menthol and cineole (target quantities of 7 and 3 mg per 4 g of drop of candy, respectively); however, the flavor solvent mixed with the menthol was varied: (1) menthol mixed with PG (2.3:1, by wt) and added to the candy separate from cineole and (2) menthol mixed with Miglyol (2.3:1, by wt) and added to the candy separate from cineole.

Hard candy was prepared in 500 g batches, which yielded 20–30 samples (free of visual defects). The sugar ingredients, 55% sucrose and 45% 42 DE corn syrup with deionized water (10% of total sugar weight), were heated to 145 °C and subsequently poured onto a marble slab, where the flavors were incorporated separately via two flavor premixes. Flavor premix 1 consisted of 7.5 g of powdered flavorless hard candy with cineole added, whereas flavor premix two consisted of 7.5 g of powdered candy but contained menthol dissolved in either PG or Miglyol. Each flavor premix was added to the candy in a separate folding step (adding one and folding to cover and melt, then adding the second and folding). After both premixes were added, the candy mass was then picked up and worked, by repeated folding, with gloved hands to fully distribute the flavor (~25 folds). Once the flavor compounds were thoroughly mixed into the candy (which had a plastic-like consistency; temperature ~70 °C), it was divided into two or three portions and molded into oval drops using a drop roller (model 93STM, Nuova Euromec). Refer to Schober and Peterson (*4*) for a more comprehensive description of the candy-making process.

Due to the volatility of the flavor compounds and the high temperature of the glass material at the time of addition, multiple batches were necessary to achieve a target concentration due to flavor evaporation. To compensate for these losses, the flavor amounts used ranged from 1.4 to 1.7 g/500 g of finished candy for menthol and from 0.5 to 0.8 g/500 g of finished candy for cineole. The flavor treatments were reformulated as necessary until batches with mean flavor quantities within ±5% of the target levels (1.75 mg of menthol and 0.75 mg of cineole/g of candy) and standard deviations within 10% were obtained.

Quantification of Volatile Flavor Compounds in Hard Candy. Menthol and cineole were quantified in treatment 1 candy (PG as solvent) by randomly selecting six candies from each batch for analysis by solvent extraction (5 mL of hexane with 1-octanal as internal standard). 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. Complete details of this method are found in Schober and Peterson (*4*).

Quantification of treatment 2 (containing Miglyol) was completed using the same extraction procedure as detailed above with the following modifications. Three grams of tricaprylin, which contained 1-octanal (1 g/L) as an internal standard, was used as the extraction solvent. After extraction, 1 g of tricaprylin layer was weighed into a 20-mL crimp-top headspace vial and analyzed by static headspace–gas chromatography analysis (same GC autosampler instrument listed above but equipped with a 1-mL headspace syringe). Each sample was incubated at 80 °C for 40 min, and 100 μL of headspace gas was injected for analysis. The same GC parameters and oven program detailed above for the liquid injection were used for headspace analysis. Peak areas were used to determine flavor concentrations through the use of a standard curve based ($r^2 = 0.99$) on menthol and cineole added to 4 g of a model candy matrix and extracted as detailed above. The standards were run in duplicates for five levels of flavor: 0.70, 3.51, 7.02, 10.53, and 14.05 μg of menthol and 0.29, 1.48, 2.95, 4.43, and 5.90 μg of cineole/4 g of candy model.

Model Aqueous System. A specialized 218-mL sealed water-jacketed vessel (inner diameter = 4.57 cm, depth = 13.34 cm, fitted with Teflon cap) was developed to monitor the release of the aroma compounds from an aqueous matrix into the air in real time. The vessel was pressurized (~4 psi) with nitrogen to produce a 20 mL/min flow rate, which split 20:1 and interfaced directly to an APCI–mass spectrometer (Quattro II, Waters, Milford, MA) via a heated transfer line (75 °C; 0.25-mm deactivated capillary column). The vessel was maintained at 38 °C under constant stirring (150 rpm). For all sample treatments the vessel was filled with 30 mL of deionized water, equilibrated to 38 °C, and 2.2 μL of the flavor compound/solutions was added under the water level via a syringe (10 μL), upon which the vessel was quickly capped and nitrogen flow initiated. All analyses were performed in triplicate.

Breath Analysis. The release of menthol and cineole from hard candy *in vivo* was studied for two panelists (number of panelists was limited by the amount of acceptable candy samples available from laboratory scale batches). As each panelist consumed a piece of candy by swirling and sucking, without chewing and keeping their mouth closed, the breath from the nose was directly and continuously sampled using a Quattro II/Micromass mass spectrometer (Waters) modified for breath analysis. 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. Ions monitored were 139 [M + H − H$_2$O]$^+$ for 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 menthol and cineole directly from the breath was determined via standard curve as described in Schober and Peterson (*4*).

Sensory Analysis. A sensory panel consisting of five judges (three females and two males), ages 24–40 years, was trained (15 practice sessions) for the time intensity (TI) study of cooling sensation from the hard candy treatments. The panelists were instructed to continually evaluate the perceived intensity of the cooling sensation for the first 4 min of sucking a candy by moving the computer cursor along a vertical line scale (0–15) on the computer monitor using a time–intensity computer software program (Compusensefive v 4.2, Guelph, ON, Canada), which was set to collect data every 0.5 s. The intensity scale was anchored at 4, 6, and 9 by three high-concentration salt solutions (cross-modality references).

The two candy treatments were evaluated in random order during four sessions (duplicates) held over a 2-day period with 4 h scheduled between same-day sessions. Candy used in both breath analysis and the time–intensity study originated from the same batch.

RESULTS AND DISCUSSION

The release kinetics of menthol dissolved in PG, Miglyol, and cineole for the model aqueous system analysis are shown
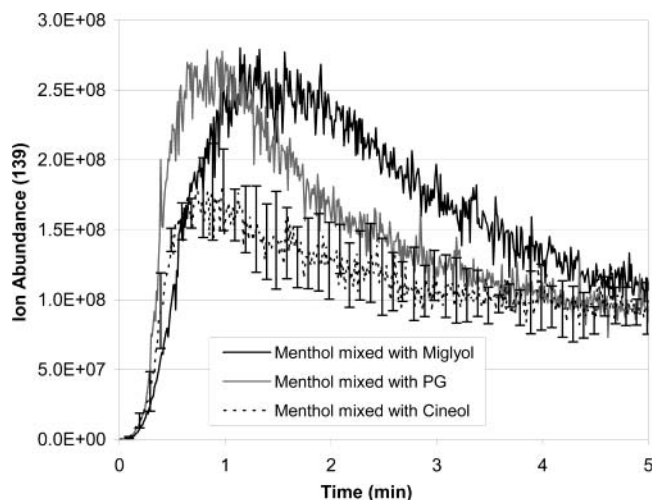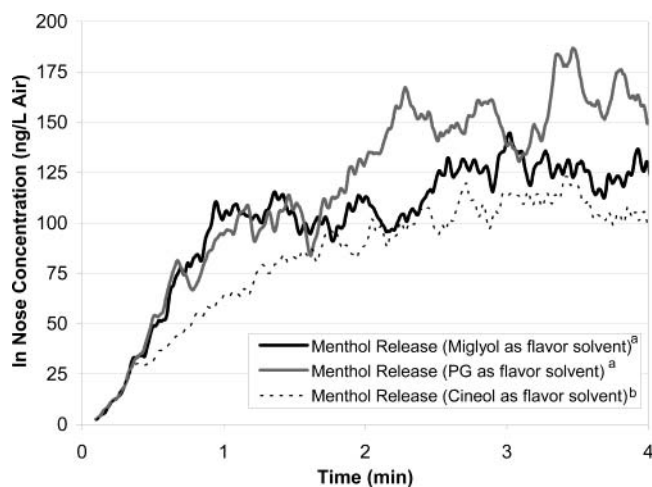
Figure 1. Influence of PG, Miglyol, or cineole as a flavor solvent on menthol release from an aqueous model system. Each curve represents the mean of three replicates (95% confidence interval displayed for the menthol mixed with cineole treatment).

a = samples also contained cineol added separate from menthol
b = data previously reported by Schober and Peterson (*1*)

Figure 2. Breath analysis release profile of menthol from hard candy comparing the two flavor solvents mixed with menthol 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 3. Breath analysis release profile of cineole from hard candy comparing the two flavor solvents mixed with menthol 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.

a = Based on 0.7, 1.1, and 1.5% salt solutions as references with intensities scaled as 4, 6, and 9, respectively

Figure 4. Comparison of perceived cooling intensity from hard candy with different flavor solvents mixed with menthol over a 4-min evaluation period. Each curve represents the average of five panelists (95% confidence interval displayed for the menthol mixed with Miglyol treatment).

in **Figure 1**. The maximum concentration of menthol reported in the headspace was significantly larger ($\sim$2-fold) for the PG and Miglyol mixtures in comparison to the cineole mixture (PG would be considered a hydrophilic solvent, whereas Miglyol and cineole are hydrophobic). As a result, the hydrophobicity of the flavor solvent was not directly correlated to the quantity of menthol released or the extent of flavor compound−flavor solvent interactions. Schober and Peterson (*4*) previously proposed that colloidal interactions may influence the volatile release properties of menthol and cineole from hard candy. Possibly, the noted differences for the menthol release properties between Miglyol (medium-chain triglyceride) and cineole (monoterpene) and the extent of the molecular interactions may be related to differences in molecular structure or even the molecular size of the flavor solvent used. Larger molecules would have a lower surface area-to-volume ratio in comparison to small molecules. A larger molecular surface area would permit more potential molecular interactions and thus may directly influence the extent of colloid formation (stability).
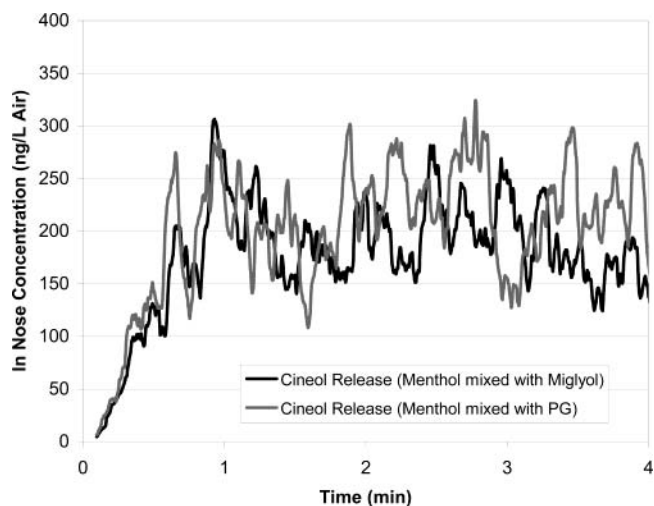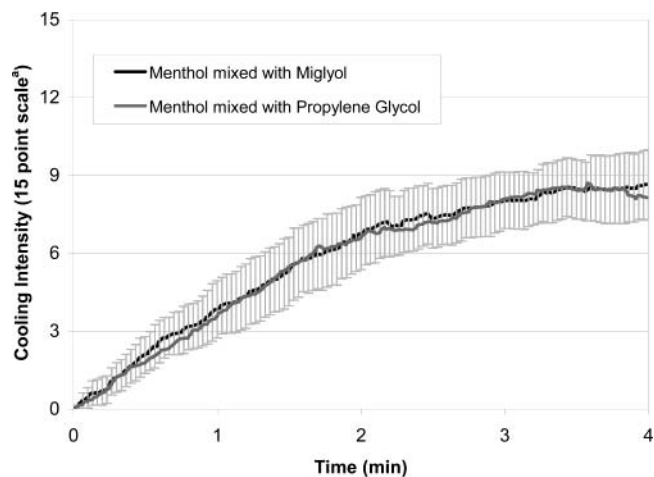
Therefore, because cineole is smaller than Miglyol, more molecular interactions between menthol and cineole may have occurred, assuming that menthol would be the surfactant in an aqueous phase with cineole or Miglyol for colloid formation (facilitate more hydrophobic contact). Small surfactant molecules have been previously reported to form micelles around hydrophobic compounds in an aqueous environment (*6*).

The hydrophobicity of the flavor solvent did, however, appear to influence the release rate of menthol, as the PG mixture was the fastest (**Figure 1**) in the aqueous model system. Because PG is water soluble, this could have resulted in a faster transport of menthol to the aqueous phase for subsequent release.

Similar results for the model aqueous system were also reported for the breath analysis, although some differences were noted. The breath analysis release profiles of menthol from PG and Miglyol for the hard candy samples are shown in **Figure 2**. The average variation of menthol release for each subject was ±27 ng/L of air (95% confidence interval; data not shown). Both PG and Miglyol had very comparable menthol release

profiles for the first 2 min of candy consumption (almost identical patterns with respect to both rate of release and "nosespace" concentration were reported), whereas there were minor differences in the last 2 min of analysis. However, the similar release rates of menthol from PG and Miglyol observed from the breath analysis were not in agreement with the model aqueous system analysis (PG release rate was faster). This discrepancy may have resulted from differences in the surface area of the flavor/flavor solvent mixture between the two analytical systems. In hard candy, the surface area of the flavor/flavor solvent mixture would be much greater (numerous small droplets) than in the model aqueous system (one droplet) and any potential differences in flavor transport to the aqueous phase (from the solvent system) may therefore have become negligible. **Figure 2** also illustrates the release of menthol when mixed with cineole as previously reported in Schober and Peterson (*4*). The panelists used for breath analysis in this study were also used in the previous study, and the data were collected over the same analysis period. The release of menthol was suppressed in the binary flavor system (when cineole was used as flavor solvent) when compared to the other two flavor solvent systems, which was analogous to the model aqueous system analysis. Thus, the choice of flavor solvent (PG, Miglyol, or cineole) did influence the release kinetics of menthol as monitored from the breath during hard candy consumption.

No differences in cineole release from the breath were found for the samples that contained the menthol/PG or Miglyol mixtures (see **Figure 3**). The cineole curves overlay one another with little variance in rate and concentration of release. Because cineole was added separately from the menthol mixtures, the extent of interactions between cineole and menthol or PG or Miglyol appeared to be negligible.

The sensory analysis furthermore indicated that there was no significant difference in the overall cooling intensity for the hard candy made with menthol dissolved in PG or Miglyol (see **Figure 4**), which would be anticipated from the menthol release properties reported by the breath analysis.

LITERATURE CITED

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