



Evaluation of equilibrium headspace concentration of orange beverage emulsion by using solid phase microextraction (SPME) during storage

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Abstract

In this study, the effect of glycerol (0.5, 1 and 1.5% w/w) and vegetable oil (2, 3 and 4% w/w) on the equilibrium headspace concentration of target volatile flavor compounds released from the orange beverage emulsions during storage was investigated by using the headspace solid phase microextraction (HS-SPME). The peak areas of 13 target orange flavor compounds (i.e. ethyl acetate, α -pinene, ethyl butyrate, β -pinene, 3-carene, myrcene, limonene, γ -terpinene, 1-octanal, decanal, linalool, nerol and geranial) composed of more than 98% of total peak area were considered as response variables. Among target volatile flavor compounds, the release behavior of β -pinene and 1-octanol was not detectable during storage. The results indicated that the equilibrium headspace concentration of target aldehyde compounds significantly ($p < 0.05$) decreased during storage depending on the type and concentration of supplementary emulsion component. In most cases, the addition of glycerol or vegetable oil to the basic emulsion formulation showed the retaining effect on the target volatile flavor compounds compared to the control sample.

Key words: Equilibrium headspace, beverage emulsion, solid phase microextraction, orange flavor compounds, relative headspace intensity.

Introduction

Flavor release is defined as a transport process of flavor compound from the matrix to the vapor phase. Flavor release is a complex phenomenon including several mechanisms: mass transfer, partitioning, matrix structural hindrance, flavor-matrix interactions, etc ¹. In fact, two major factors control the rate of aroma release from products, namely the volatility of the aroma compounds in the product base (thermodynamic factor) and the resistance to mass transfer from product to air ². Partition represents a fundamental parameter describing the distribution of a volatile flavor compound between two phases at equilibrium. Partition coefficient and mass transfer of volatile flavor compounds depend on the structure/composition of food stuff, temperature and flavor binding ^{1,3}.

The release of volatile essences from the emulsion system is an issue of high relevance in food technology and food colloids science. Flavor-cloud beverage emulsions are widely used emulsions in the beverages and soft drinks (e.g., citrus drinks) to give the products an opaque appearance and desirable aroma. Although the emulsions have a low oil concentration, the addition of a flavor-cloud emulsion changes the properties of the beverage phase, thus altering volatile compound partition. As a result, the aroma profile above the product changes and this may affect the overall perceived flavor ⁴. The release of volatile flavor compounds from the beverage emulsions is also very critical issue during processing and storage. Thus, a combination of experience and science is applied by the flavorists in order to adjust flavor formulations to compensate for the type of cloud emulsion.

Quantitative analysis of key volatile compounds in the orange beverage emulsion plays an important part in evaluating their freshness in the emulsion based-products (i.e. soft drink). The release intensity of key volatile flavor compounds (i.e. esters, monoterpenes, aldehydes and alcohols) released from the orange beverage emulsion during storage are important in determining the overall quality and acceptability of the emulsion system to maintain the aroma prior to the consumption in the soft drink. As illustrated by Fechner's law, the perceived aroma intensity is logarithmically related to the headspace concentration of the volatile compound ⁵. The physicochemical behavior of small molecules such as flavor compounds in the matrix and headspace of food stuff is one of the most important parameters involved in their activity and sensory perception; hence, this behavior can have pronounced effects on the flavor quality of foods which are mostly emulsions, i.e. dispersed systems of oil and aqueous phases ⁶. The interactions between flavor compounds and emulsion components change the affinity of the volatile flavor compounds for the emulsion phases by modifying the nature and the number of free binding sites. Therefore, the knowledge on the effect of main emulsion components on the equilibrium headspace concentration of the volatile flavor compounds can be useful for developing the pre-formulation of a beverage emulsion with the controlled flavor release.

The main objective of present study was to investigate the effect of glycerol (0.5, 1 and 1.5% w/w) and vegetable oil (2, 3 and 4% w/w) contents on equilibrium volatile headspace concentration of orange

beverage emulsion during storage. In this study, the headspace solid-phase microextraction (HS-SPME) method developed in our previous study ⁷ was used for measuring the equilibrium headspace concentration of target volatile flavor compounds released from the orange beverage emulsions. HS-SPME has also been used as a fast alternative technique to determine the flavor release by previous researchers ⁸⁻¹⁰. The preliminary study indicated that the addition of glycerol and vegetable oil over the concentration levels mentioned earlier led to undesirable changes in flow behavior, polydispersity index, density and pH of the beverage emulsion. Thus, the effect of given concentration levels of glycerol and vegetable oil on the equilibrium volatile headspace concentration of orange beverage emulsion was investigated during six months storage.

Materials and Methods

Materials: Orange volatile compounds, ethyl acetate (99%), α -pinene (99.5%), ethyl butyrate (99.7%), β -pinene (98.5%), 3-carene (98.5%), myrcene (95%), limonene (99%), γ -terpinene (98.5%), octanal (98%), decanal (95%), linalool (95%), 1-octanol (95%) and citral (95%) (neral and geranial) were supplied by Fluka (Buch, Switzerland). Arabic gum (food grade) was provided by Colloides Naturels International Co. (Rouen, France). Xanthan gum was donated by CP Kelco (San Diego, CA, USA). Glycerol (98.5%) was provided by BDH Ltd. (Poole, Dorset). Citric acid, sodium benzoate and potassium sorbate (p.a. $\geq 95\%$) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Valencia cold pressed orange oil was provided by Danisco (Aarhus, Denmark). Vegetable oil was purchased from a local retailer.

Preparation of orange beverage emulsion: A representative orange beverage emulsion composed of Arabic gum (20% w/w), xanthan gum (0.3% w/w), orange oil (14% w/w), sodium benzoate (0.1% w/w), potassium sorbate (0.1% w/w), citric acid (0.4% w/w) and deionized water was prepared as a control sample. The other orange beverage emulsions were also formulated based on the basic emulsion formulation (or control sample), but containing either different concentration of glycerol (0.5, 1 and 1.5% w/w) or vegetable oil (2, 3 and 4% w/w) depending on the target emulsion formulation. To prepare the continuous phase, sodium benzoate, potassium sorbate and citric acid were dispersed sequentially in deionized water (60°C) using a high shear mixer (Waring Blender 32BL80, Torrington, CT, USA). While mixing the mixture, Arabic gum was gradually added to the deionized water (60°C) and mixed for 3 min to facilitate hydration. The Arabic gum solution was kept overnight at room temperature to fully hydrate ¹¹.

Xanthan gum solution was also prepared separately by dissolving xanthan gum powder in deionized water and then mixed with Arabic gum solution by using the high speed mixer. For glycerol-based beverage emulsions, glycerol was added to the continuous phase (water phase). While mixing the continuous phase, the cold pressed orange oil was gradually added as dispersed phase (oil phase) into the continuous phase to provide an initial coarse emulsion. For vegetable oil-based beverage emulsions, dispersed phase was prepared by mixing orange oil and vegetable oil and then it was added to the continuous phase. Fine emulsification (i.e. small droplet size of smaller than 1 μm and narrow droplet size distribution) was achieved by subjecting pre-emulsions to pre-homogenization using high shear homogenizer (Silverson L4R, Buckinghamshire, UK) for 1 min and then passed

through a high-pressure homogenizer (APV, Crawley, UK) for three passes (30, 28 and 25 MPa).

HS-SPME analysis: The SPME device, SPME fiber assortment kit No. 4, 20 ml glass vial, Teflon coated rubber septa and aluminum caps were supplied by Supelco Inc. (Bellefonte, PA, USA). As shown in our previous study ⁷, the extraction procedure using a carboxen/polydimethylsiloxane (75 mm, CAR/PDMS) fiber at 25°C for 45 min under stirring mode provided the highest extraction efficiency for orange beverage emulsion. In the present study, 10 g concentrate orange beverage emulsion was transferred into a 20 ml serum vial. Subsequently, the vial was sealed with a Teflon-lined septa and screw cap that was immersed in a thermostated water-bath (25°C). After 10 min equilibrium time period, the SPME fiber coated with CAR/PDMS was manually exposed to the sample headspace for 45 min at 25°C under stirring mode to reach the equilibrium condition. Consequently, the fiber was immediately inserted into the injector of gas chromatography (GC) system for thermal desorption at 250°C for 8 min. Each experiment was carried out in duplicate and the average of two individual sampling was reported for data analysis. Samples were taken at regular time intervals (once per two months) during six months of storage. The static headspace concentration was monitored in order to determine the effect of main emulsion components on the equilibrium headspace concentration of the target flavor compounds.

GC condition: As mentioned in our previous study ⁷, the volatile flavor compounds of Valencia cold pressed orange oil were initially identified by using a Hewlett-Packard 6890N GC system (Wilmington, DE, USA) equipped with Time-of-Flight Mass Spectrometer (TOFMS, Pegasus III, Leco Corp., St. Joseph, MI, USA). The volatile flavor compounds of orange beverage emulsions were then analyzed by a Hewlett-Packard 6890 GC equipped with a flame ionization detector (FID) (J & W Science, Folsom, CA, USA), DB-Wax column (30 m x 0.25 mm i.d.; 0.25 μm film thickness; Supleco, MA, USA). The GC injection port was equipped with a 0.75 mm i.d. liner (Supelco) to minimize peak broadening. For GC-FID analyses, the injection was performed for 5 min at 250°C in the splitless mode. Oven temperature was programmed at 45°C for 5 min, then ramped to 51°C at 1°C/min and held for 5 min at 51°C, then increased to 160°C at 5°C/min and finally raised to 250°C at 12°C/min and held for 15 min at the final temperature. Helium was used as the carrier gas. Detector temperature was set at 270°C. The experimental conditions have been described in detail in our previous study ⁷.

Data analysis: Experiments were performed according to a completely randomized design (CRD). The individual significance probability of each independent variable is shown by p-value. The p-value provides an objective measure of the strength of evidence which the data supplies in favor of the null hypothesis. A small p-value provides evidence against the null hypothesis, because data have been observed that would be unlikely if the null hypothesis were correct. All data were subjected to analysis of variance (ANOVA) using the Minitab v. 13.2 statistical package (Minitab Inc., State College, PA, USA). Least significant difference (LSD) tests were used to compare differences among means for data analysis.

Results and Discussion

Preliminary study: According to our previous study ⁷, the main volatile flavor compounds were identified by GC/MS and quantified by GC-FID in Valencia cold pressed orange oil composed. More than 98% of the total flavor compounds composed of monoterpene hydrocarbons (i.e. α -pinene, β -pinene, 3-carene, myrcene, limonene and γ -terpinene), esters (i.e. ethyl acetate and ethyl butyrate), alcohol (i.e. linalool and 1-octanol) and aldehyde compounds (i.e. octanal, decanal, neral and geranial) (Table 1). These flavor compounds were identified as the representative flavor compounds of cold pressed orange oils by previous researchers ^{12, 13}. Thus, the peak area of target volatile flavor compounds and total flavor compounds were considered as response variables in this study.

Equilibrium volatile headspace concentration: Among 14 target volatile flavor compounds, the changes in equilibrium headspace concentration of β -pinene and 1-octanol were not detectable during storage. This observation may be explained not only by their small quantity but also by the interaction between the emulsifiers and these flavor compounds. As stated by previous study ⁴, emulsifiers can interact with volatile compounds either through a binding effect or by changing the mass transport properties of the liquid interfacial boundary layer. In fact, the negative effect of hydrocolloids on the volatile headspace concentration may be explained by the specific binding interaction of the small flavor compounds as a result of adsorption, complexation, physical entrapment, encapsulation and hydrogen bonds ^{3, 14}. The beverage emulsions composed of different supplementary emulsion components showed significant ($p < 0.05$)

Table 1. Volatile flavor compounds of Valencia cold pressed orange oil identified by using HS-SPME-GC-MS.

Compound	Similarity	Retention time (s)	Unique mass	Formula	FID area (%)
Ethenyl acetate,	954	95.481	44	C ₄ H ₆ O ₂	tr.
Ethyl acetate	793	196.348	31	C ₄ H ₈ O ₂	0.1
Ethyl propanoate	978	201.082	57	C ₅ H ₁₀ O ₂	tr.
α -Pinene	951	275.944	93	C ₁₀ H ₁₆	0.03
3-Methoxyhex-1 ene	913	293.382	60	C ₇ H ₁₄ O	tr.
2-Undecen-4-ol	891	298.182	71	C ₁₁ H ₂₂ O	tr.
Ethyl butyrate	949	307.294	73	C ₆ H ₁₂ O ₂	1.1
β -Pinene	929	472.195	93	C ₁₀ H ₁₆	0.04
3-Carene	931	548.821	93	C ₁₀ H ₁₆	0.16
Myrcene	885	616.504	93	C ₁₀ H ₁₆	1.2
(S)- cinene or carvene,	853	714.349	79	C ₁₀ H ₁₆	tr.
Cyclohexene, 1-methyl-5-(1-methylethenyl)-	888	717.616	79	C ₁₀ H ₁₆	tr.
Cyclohexene, 4-methyl-1-(1-methylethenyl)-	761	721.408	32	C ₁₀ H ₁₆	tr.
Methyl 2-butynoate,	812	723.127	27	C ₅ H ₆ O ₂	tr.
Limonene	911	748.768	93	C ₁₀ H ₁₆	94.9
1,8-Cineole	949	785.193	93	C ₁₀ H ₁₈ O	tr.
Camphene	629	789.146	91	C ₁₀ H ₁₆	tr.
γ -Terpinene	917	810.577	93	C ₁₀ H ₁₆	0.41
p-Cymene	879	818.923	46	C ₁₀ H ₁₄	tr.
3,5-Dimethylanisole	793	894.782	91	C ₉ H ₁₂ O	tr.
Octanal	842	1109.43	43	C ₈ H ₁₆ O	0.03
Limonene oxide, cis-	967	1660.58	43	C ₁₀ H ₁₆ O	tr.
Linalool tetrahydride,	793	1689.58	69	C ₁₀ H ₂₂ O	tr.
Limonene oxide, trans-	928	1690.98	43	C ₁₀ H ₁₆ O	tr.
R)-(+)-citronellal	908	1756.13	41	C ₁₀ H ₁₈ O	tr.
Copaene	706	1759.73	43	C ₁₅ H ₂₄	tr.
Cyclododecanol	805	1798.18	67	C ₁₂ H ₂₄ O	tr.
Decanal	952	1819.12	57	C ₁₀ H ₂₀ O	0.12
2,4-Dimethyl-1-penten-3-ol	763	1906.93	39	C ₇ H ₁₄ O	nd
(E)- Geranyl methyl ether	725	1909.13	55	C ₁₁ H ₂₀ O	nd
2-Methyl-1,5-heptadien-4-ol	741	1909.78	107	C ₈ H ₁₄ O	nd
Hexanol	794	1913.87	44	C ₆ H ₁₄ O	tr.
2,7-Octadiene-1,6-diol, 2,6-dimethyl-, (E)-	857	1927.1	28	C ₁₀ H ₁₈ O ₂	tr.
Linalool	940	1930.20	93	C ₁₀ H ₁₈ O	0.36
α -Terpineol	948	1948.73	59	C ₁₀ H ₁₈ O	tr.
1-Octanol	895	1949.11	56	C ₈ H ₁₈ O	0.06
Neral	944	2128.13	41	C ₁₀ H ₁₆ O	0.03
Geranial	874	2203.74	69	C ₁₀ H ₁₆ O	0.05
6-Octen-1-ol, 3,7-dimethyl-	955	2261.36	67	C ₁₀ H ₂₀ O	tr.
Octanoic Acid	894	2599.77	60	C ₈ H ₁₆ O ₂	tr.
Sorbic Acid	932	2663.43	97	C ₆ H ₈ O ₂	tr.
n-Decanoic acid	862	2737.12	60	C ₁₀ H ₂₀ O ₂	tr.
1-Butanol, 4-methoxy-	749	2907.13	32	C ₅ H ₁₂ O ₂	tr.
Hexagol	844	2922.51	32	C ₁₂ H ₂₆ O ₇	tr.
2-Propanol,1-(1-methylethoxy)-	773	3004.25	59	C ₆ H ₁₄ O ₂	tr.

differences in static equilibrium headspace. In fact, the equilibrium volatile headspace concentration of orange flavor compounds was significantly ($p < 0.05$) influenced by the type and concentration of supplementary emulsion component depending on the characteristics of flavor compound (e.g. solubility, hydrophobicity, volatility, etc.). This observation may be explained by the interaction between the main emulsion components and target flavor compounds.

As a general rule, the addition of polar or water-soluble component to the emulsion formulation would increase the equilibrium headspace concentration of oil-soluble volatile compounds vice versa polar or water soluble flavor compounds. It is well known that the addition of vegetable oil to the emulsion formulation alters the volatility and/or partitioning of polar or water soluble-flavor compounds. Hence, the flavor partitioning of polar volatile compounds from the sample into the vapor phase (headspace) tend to become high with increasing the vegetable oil content in the dispersed phase^{4, 15} demonstrated that the partition of volatiles in cloud emulsions was estimated as a function of lipid content. They showed greater retention of hydrophobic compounds with increasing lipid content. In agreement with previous study, the addition of vegetable oil resulted in the decreased equilibrium headspace concentration of orange flavor compounds in most cases.

Effect of glycerol and vegetable oil on the equilibrium headspace concentration of esters: It was shown that all beverage emulsions exhibited almost the same change pattern in term of ethyl acetate during storage. In all cases, except for the beverage emulsions containing 0.5% and 1.5% (w/w) glycerol, the equilibrium headspace concentration of ethyl acetate significantly ($p < 0.05$) increased during 4 months of storage. Subsequently, the equilibrium headspace concentration of ethyl acetate significantly ($p < 0.05$) decreased during the last two months of storage (Fig. 1a). The equilibrium headspace concentration of ethyl butyrate originally depended on type of supplementary emulsion component. It was observed that the addition of glycerol led to a significant ($p < 0.05$) change in the equilibrium headspace concentration of ethyl butyrate, compared to the control sample. Conversely, the presence of vegetable oil in the basic emulsion formulation resulted in the same effect pattern compared to the control sample. In general, the equilibrium headspace

concentration of ethyl butyrate was observed to be significantly ($p < 0.05$) decreased in all beverage emulsions, except for glycerol-based beverage emulsions (Fig. 1b).

Effect of glycerol and vegetable oil on the equilibrium headspace concentration of monoterpene hydrocarbons: In term of α -pinene, the addition of 0.5% (w/w) glycerol did not significantly ($p > 0.05$) change the equilibrium volatile headspace concentration except for the last two months of storage, compared to the control sample. The beverage emulsion containing 1% (w/w) glycerol showed the same release pattern as the beverage emulsions containing 3% and 4% (w/w) vegetable oil. On the other hand, the similar release pattern for α -pinene was also observed by the comparison of beverage emulsion containing 1.5% (w/w) glycerol and the one containing 2% (w/w) vegetable oil (Fig. 2a). In these emulsions, the equilibrium headspace concentration of α -pinene significantly ($p < 0.05$) decreased within the first and last two months of storage. Conversely, an increase in the equilibrium headspace concentration of α -pinene was shown by the beverage emulsions containing 1.5% (w/w) glycerol and 2% (w/w) vegetable oil during three to four months of storage. The same observation was observed by the control sample. However, the equilibrium headspace concentration of α -pinene indicated an increase during the last two months of storage.

The equilibrium headspace concentration of 3-carene appeared to be significantly ($p < 0.05$) decreased in all samples during storage in almost all cases. The orange beverage emulsions containing 1.5% (w/w) glycerol and 2% (w/w) vegetable oil showed an increase in the equilibrium headspace concentration of 3-carene during three to four months of storage. The same observation was observed for the beverage emulsion containing 4% (w/w) vegetable oil during the last two months of storage. The results indicated that the change in the equilibrium headspace concentration of myrcene during storage. The addition of 0.5% and 1% (w/w) of glycerol did not significantly ($p > 0.05$) change the release pattern of myrcene, compared to the control sample (Fig. 2b). On the other hand, the orange beverage emulsion containing 1.5% (w/w) glycerol had the same release pattern as the vegetable oil-based beverage emulsions in term of myrcene. In these emulsions, the equilibrium headspace concentration of myrcene was found to be significantly ($p < 0.05$) decreased during the first two months of storage; while an increase in the equilibrium

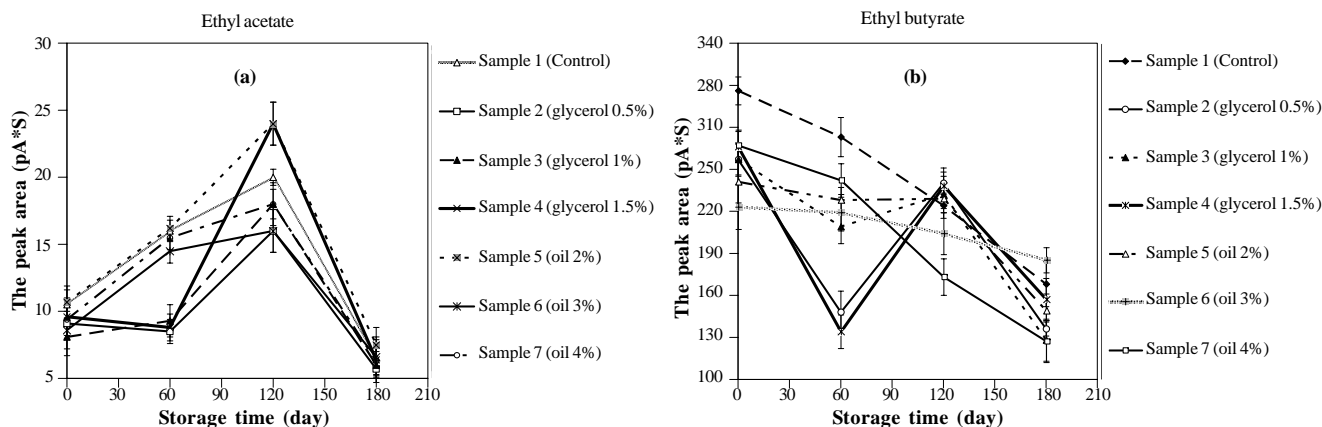


Figure 1. The changes in equilibrium headspace concentration of ethyl acetate (a) and ethyl butyrate (b) during storage period as function of glycerol and vegetable oil contents.

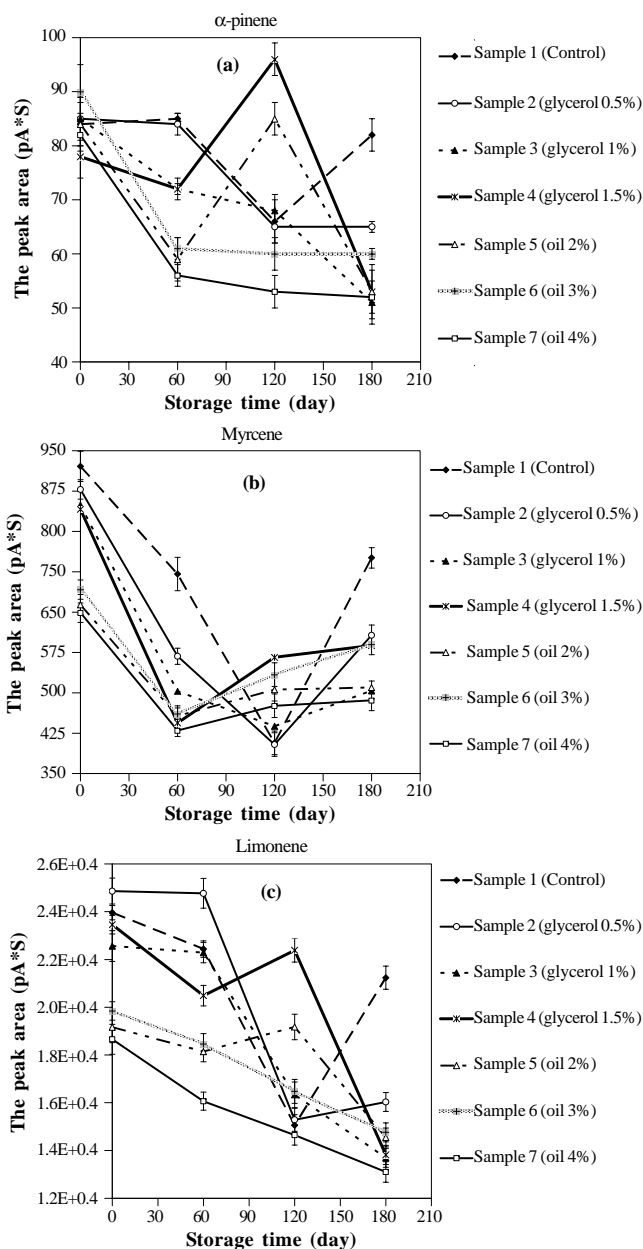


Figure 2. The changes in equilibrium headspace concentration of α -pinene (a), myrcene (b) and limonene (c) during storage period as function of glycerol and vegetable oil contents.

headspace concentration of myrcene was observed during the last four months of storage (Fig. 2b).

It was found that the orange beverage emulsion exhibited almost the same equilibrium release pattern in terms of α -pinene and limonene (Figs 2a and 2c). The equilibrium headspace concentration of limonene significantly ($p < 0.05$) decreased in most cases during storage. The decrease of limonene content may be reflected by the fact that limonene is broken down to α - or β -terpineol through an acid catalyzed hydration¹⁶. It should be noted that α -terpineol contributes negatively to orange flavor, while β -terpineol is believed as pungent, earthy or woody aroma¹⁷. The equilibrium headspace concentration of γ -terpinene followed a decrease behavior in most cases, except for the samples

containing 1% and 1.5% (w/w) glycerol during the first four months of storage, respectively.

Effect of glycerol and vegetable oil on the equilibrium headspace concentration of alcohols: As mentioned earlier, the equilibrium headspace concentration of 1-octanol was not obviously detectable during storage. On the other hand, the equilibrium headspace concentration of linalool was markedly influenced by type of supplementary emulsion component added to the basic emulsion formulation. A significant ($p < 0.05$) decrease in the equilibrium headspace concentration of linalool in the control sample was observed during storage (Fig. 3). On the other hand, an increase in the equilibrium headspace concentration of linalool was observed for the orange beverage emulsions prepared by 0.5% and 1% (w/w) glycerol during the first two months of storage (Fig. 3). In general, the addition of vegetable oil led to a decrease in the equilibrium headspace concentration of linalool before storage test. Conversely, a significant ($p < 0.05$) increase in the equilibrium headspace concentration of linalool was observed by the vegetable oil-based beverage emulsions in most cases. This observation may be attributed to the degree of hydrophobicity and/or solubility of linalool into the water phase (glycerol), compared to the oil phase (vegetable oil).

Effect of glycerol and vegetable oil on the equilibrium headspace concentration of aldehydes: Fig. 4a indicates that the addition of both supplementary emulsion components led to a significant ($p < 0.05$) decrease in the equilibrium headspace concentration of octanal during six months of storage. This observation may be explained by the fact that octanal presumably is oxidized to the corresponding acid¹⁸. On the other hand, the control sample showed a significant ($p < 0.05$) increase in the equilibrium headspace concentration of octanal during the last two months of storage.

The control sample showed a significant ($p < 0.05$) decrease in the equilibrium headspace concentration of decanal during the storage period (Fig. 4b). As also observed in glycerol-based beverage emulsions, the addition of glycerol did not significantly ($p > 0.05$) change the release pattern of decanal, compared to the control sample. Conversely, the presence of vegetable oil significantly ($p < 0.05$) increased in the equilibrium headspace concentration of decanal during the last two months of storage

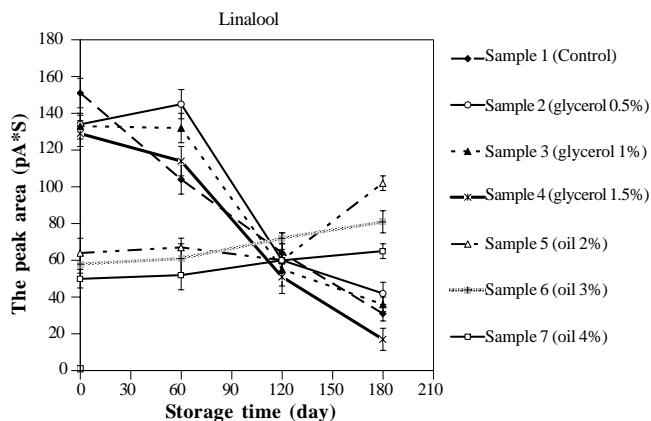


Figure 3. The changes in equilibrium headspace concentration of linalool during storage period as function of glycerol and vegetable oil contents.

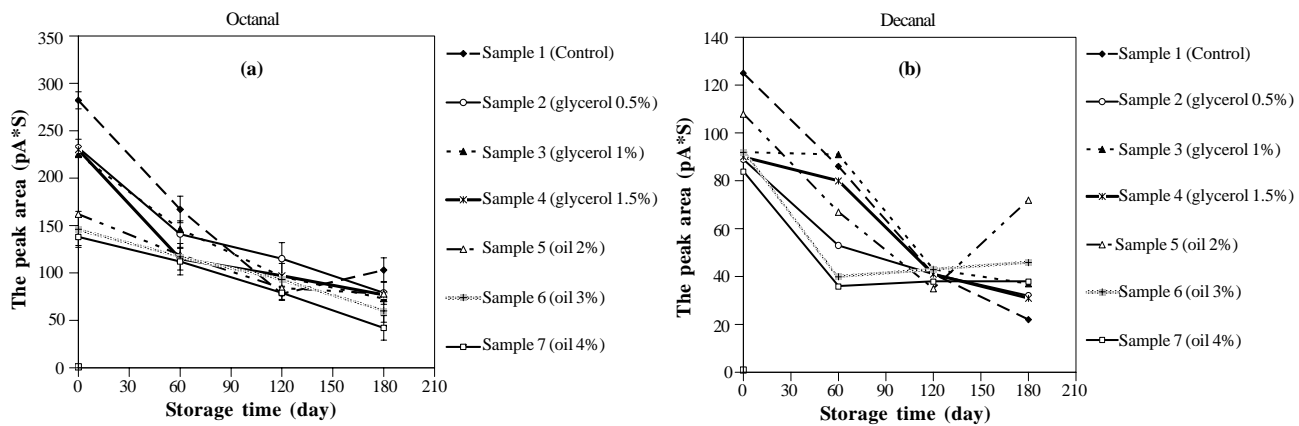


Figure 4. The changes in equilibrium headspace concentration of octanal (a) and decanal (b) during storage period as function of glycerol and vegetable oil contents.

(Fig. 4b). However, the decrease in the equilibrium headspace concentration of decanal was also observed by the oil-based beverage emulsions during the first two months of storage. The addition of different concentration of glycerol did not significantly ($p>0.05$) influence the release pattern of decanal (Fig. 4b). In all beverage emulsions, the equilibrium headspace concentration of neral significantly ($p<0.05$) decreased during storage. It was found that the equilibrium volatile headspace concentration was clearly affected by the concentration of supplementary emulsion component. All orange beverage emulsions showed a significant ($p<0.05$) decrease in the equilibrium headspace concentration of geranial during storage.

Overall equilibrium headspace concentration: In term of total flavor compounds, the addition of vegetable oil resulted in the decreased overall equilibrium headspace concentration, compared to the control sample (Fig. 5). Carey *et al.*⁴ also found that the oil fraction (i.e., the relative amount of oil to water) was the key factor influencing flavor release. All orange beverage emulsions also exhibited almost the same overall release intensity as limonene. This observation may be explained by the reason that limonene was composed of more than 94% of total volatile flavor compounds in Valencia cold pressed orange oil.

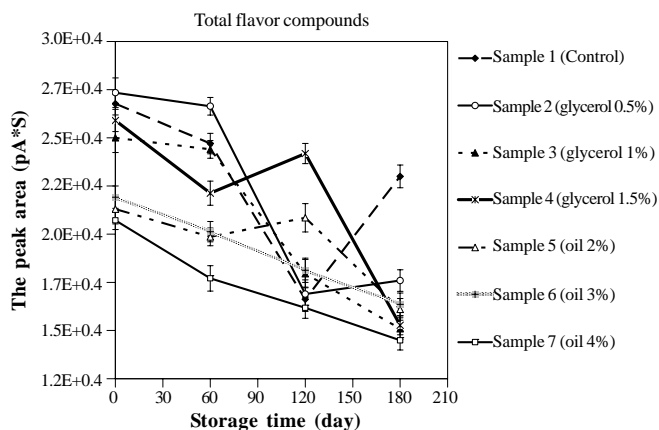


Figure 5. The changes in overall equilibrium headspace concentration of target flavor compounds during storage period as function of glycerol and vegetable oil contents.

It should be noted that ethyl acetate (fruity like), α -pinene (fruity, piney like), ethyl butyrate (fruity, sweet like), β -pinene (musty, green like), myrcene (musty, geranium like), limonene (licorice, citrusy like), γ -terpinene (citrusy, terpeny like), octanal (citricy, green like), decanal (citricy, fatty like), linalool (floral like), neral (citrus, musty like) and geranial (lemon, minty like) contribute positively to the fresh orange aroma^{13,17}. As also stated by Ohta *et al.*¹⁹, the oxygen-containing components, including aldehydes such as octanal and alcohols are considered as the ‘character impact compounds’ or major contributors to the fresh and pleasant orange aroma because of their low threshold and olfactory characteristics. Thus, the changes in the sensory properties, organoleptic attributes and overall acceptability of orange emulsion-based product (i.e. soft drink) over time could be explained by the changes in release intensity and pattern of representative orange aroma compounds.

Conclusions

In the present work, the change patterns of the equilibrium headspace concentration of target volatile flavor compounds released from the orange beverage emulsions were investigated during storage. As compared to the control sample, the presence of glycerol or vegetable oil in the basic emulsion formulation significantly ($p<0.05$) changed the equilibrium headspace concentration of target flavor compounds released from the orange beverage emulsions containing glycerol or vegetable oil. In most cases, the addition of glycerol or vegetable oil to the beverage emulsion formulation resulted in the flavor retention, compared to the control sample. This retaining effect of glycerol or vegetable oil may be due to the positive effect of glycerol or vegetable oil on the solubility of some of target flavor compounds such as aldehyde compounds studied. In fact, the increased solubility of such volatile flavor compounds led to the subsequent reduction in their equilibrium headspace concentration. However, the present study did not obviously highlight this matter. In general, the equilibrium headspace concentration of aldehyde volatile compounds (i.e. octanal, decanal, neral and geranial) decreased during storage. Although the prepared beverage emulsions contained the same proportion of orange oil, but the overall equilibrium headspace concentration of volatile flavor compounds released from vegetable oil-based beverage emulsions was less than that of released from the control sample and glycerol-based

beverage emulsions in most cases. It was concluded that the differences observed among the equilibrium headspace concentration of the beverage emulsions could be described by the different matrix structures induced by glycerol and vegetable oil leading to the different interactions between volatile flavor compounds and main emulsion components.

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