Novel Non-beer Flavor Applications of Hop Oil Fractions

Application in fruit, beverage, dairy, savory and other categories

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Humulus lupulus, more commonly called hops, have been used almost exclusively in the brewing of beer for centuries. Hops provide bitterness, aroma, foam stability and act as a preservative in beer.

The soft resins found in the lupulin glands of the female cone contain the hop acids which are used to impart bitterness to beer. The essential oil in the lupulin glands provides the aroma or spicy flavor to beer.

Hops are harvested in late August or early September. During harvesting the hop cones are stripped from the vine and dried to about 3–5% moisture. The dried cones are then baled or milled and pelletized. Though most breweries use pelletized hops in the brewing of beer, increasingly many breweries are enjoying the advantages of brewing with hop extracts. Hop pellets are routinely extracted with liquid CO_2 at about 2,400–3,400 psi and 40–55°C. The CO_2 extract contains α- and β-acids and essential oils. Most extracts contain about 40% α-acids, an equivalent amount of β-acids, and 10–15% hop oil by weight. The hop acids can be removed from the extract and separated. Further processing can yield modified hop acids extracts. These modified hop acids extracts can be used to improve brewing efficiencies, deliver specific bitter taste profiles and provide foam enhancement and/or light stability in beer. The hop essential oil remains behind in the extract, which also contains chlorophylls, waxes, fats and other uncharacterized resins.

Codistillation with water, or hydrodistillation, is an effective way to remove the hop essential oils from the extract. Hop oils can then be fractionated into distinct products with different compositions and flavor profiles. This paper characterizes five distinct hop oil fractions using GC/MS and sensory analysis. These observations are used to make prototype non-beer flavors containing these hop oil fractions. Finally, the application of hop oil fractions to non-beer flavors is discussed.

Production of Hop Oil Fractions

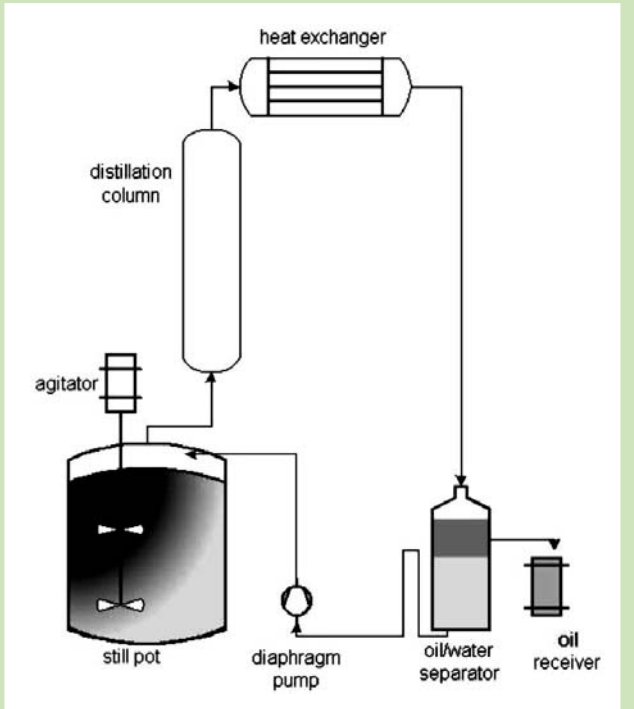
Typically, 2,000-gallon stainless steel stills are used to distill hop essential oils. Approximately 800 gallons of water are combined with 3,600 pounds of acid-free hop extract. At ambient pressures the water/oil begins to distill at 100°C. It is possible to make cuts or take fractions as compounds with higher vapor pressure begin to distill off. Different fractions can be monitored using a refractometer to measure the change in refractive index. Gross cuts are collected based on their refractive index as light, intermediate or heavy fractions. These fractions are then fractionated again in smaller high vacuum stills based on their boiling point. **F-1** depicts the equipment used to fractionate hop oils.[a]

Sensory

A non-interfering base that could simulate sweet and savory applications was needed to test the hop fractions. Each of the five fractions was presented to the panel in distilled water (DI water), a savory base and a sweet base. The savory base consisted of 3 g salt plus 0.5 g monosodium glutamate (MSG) for every 1,000 g of water. The sweet base consisted of 60 g of sugar and 0.5 g citric acid for every 1,000 g of water. Hop oil fractions A, B and C were dosed at 2 ppm for tasting, while fractions D and E were dosed at 1 ppm. Samples were made 1–2 hours

[a]Hop oil fractions used in this study were manufactured by Kalsec Inc.

Hop oil fractionating equipment **F-1**



before sensory evaluation and were served at room temperature. Each panelist received approximately 1 oz of each sample in a soufflé cup. The panelists were not made aware of the nature of the flavoring materials they were describing.

Sensory Evaluation

Descriptive panelists (n = 12–15) trained using a modified spectrum methodology on a 0–15 universal scale evaluated five hop fractions in the three bases referred to above. Panelists evaluated each blind coded sample individually, discussed attributes as a group and rated attributes individually. Panelists were allowed to cleanse their palates with distilled water or crackers, as needed.

Analytical

Hop oil fraction A was analyzed by GC/MS using a Thermo-Finnigan Trace GC and Polaris Q MS. Samples were diluted at 1% in acetone before being injected into a hot injector (220°C). GC temperature gradient was 80°C (hold 5 min) to 240°C at 12°C/min (hold 20 min), with helium used as carrier gas at 1 mL/min. A Supelco fused silica wax column (30 m x 0.25 mm ID; 0.25 µm film) was used for separation of the volatile compounds.

Hop oil fractions B–E were analyzed by GC/MS using a Varian 3800 GC and Varian Saturn 2000 MS. Samples were diluted at 1% in acetone before being injected into a hot injector (220°C). GC temperature gradient was 60–240°C at 3°C/min, with helium used as carrier gas (14 psi). A Supelco fused silica SLB-5ms column (30 m x 0.25 mm ID; 0.25 µm film) was used for separation of the volatile compounds.

Flavor Creation

The flavor chemist used the information gathered by the analysis of hop fractions to make prototype flavors.

Flavors With and Without Hop Oil

Herein are the authors' tasting notes on comparison of flavors made with and without hop oil fractions.

Hop fraction	Flavor	Control (without hops)	With hops
A	Coconut	**T-4.1** • Coconut, lactones • Waxy, fatty, pronounced plastic/ chemical, artificial • Coconut, pineapple, sweet • Fatty, coconut, sweet, unpleasant/ artificial • Coconut, vanilla, waxy, fatty	**T-4.2** • More depth, brown note, more rounded, husk, woody, natural • Greener, fatty, fruity, tropical fruit character, sweet • Added mango, tropical fruit • Same flavors, not as strong, still unpleasant • Green, more balanced, natural flavor
B	Raspberry	**T-5.1** • Candylike • Sweet, berry, intense • Sweet, spicy, green, synthetic, berry • Berry, β-ionone	**T-5.2** • More natural, better mouthfeel • Greener, herbal, preferred, more real • Greener, viney, raspberry, more rounded • Same • Viney, green, not so berrylike, improved mouthfeel, more natural
B	Roast garlic	**T-5.3** • Garlic, roast • Salty, savory, slight garlic • Garlic, rubbery, green, pungent, salty • Salty, garlic • Garlic, roasted, salty	**T-5.4** • Reduced garlic intensity, low green • More garlic, brown, roasted • No difference • Salty, garlic, brings up roasted character • Brown flavor, more roasted, garlic bread
C	Root beer	**T-6.1** • One-dimensional—methyl salicylate • Menthol, sweet, vanilla, root beer aroma • Root beer, sweet, licorice • Vanilla, root beer (A&W profile, specifically)	**T-6.2** • Woodier, more depth and mouthfeel, less cloying • Deeper flavor, woody, more natural root beer • Greener, mint, less root beer, improvement • Not as root beerlike, more mintlike • Vanilla, more mint, lower root beer, cedar/woody

Flavors were made with and without a hop oil fraction. The authors tasted the flavors in an appropriate base, and described the differences between the pairs of flavors with and without hop oil fractions.

Discussion of Sensory Results

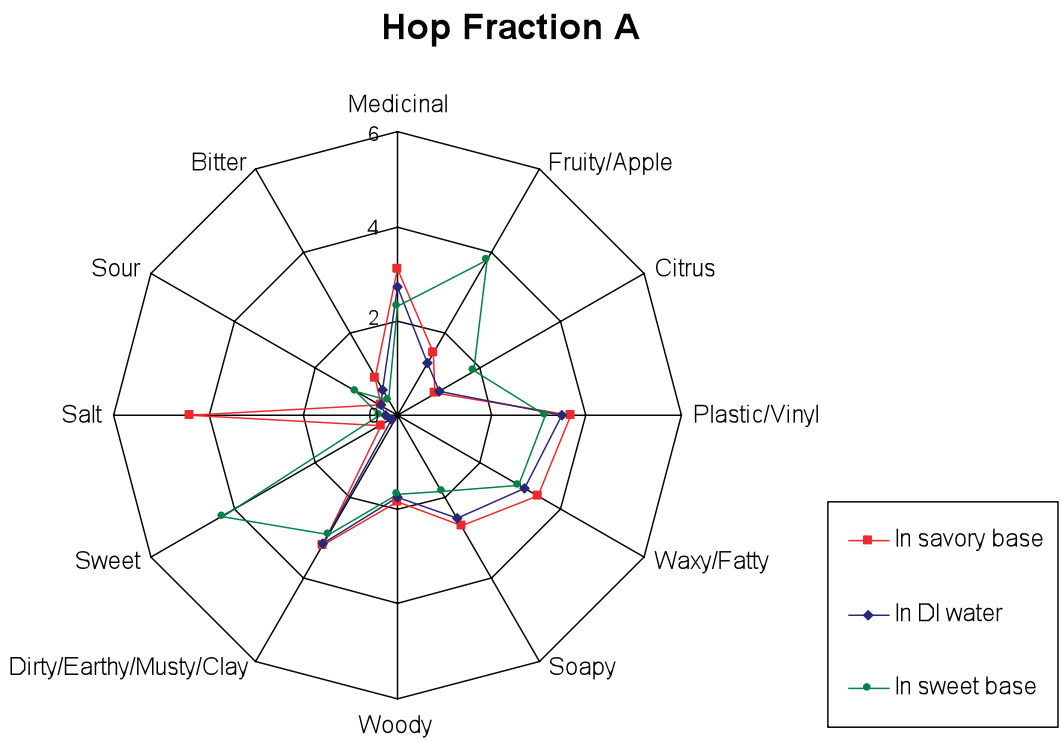
F-2–6 show descriptive sensory profiles developed by trained panelists of each hop fraction. The hop fractions were tasted in the sweet base, savory base and distilled water. Often the different bases amplified attributes specific to sweet or savory applications. Hop fraction A was described by the panel as being plastic, waxy, fatty, soapy and medicinal. The addition of fraction A to the sweet base significantly increased the fruity, apple and citrus characteristics. Fraction B was fruitier and described as circus peanut (confection), banana, tropical, citrus, dirty and woody. The addition of fraction B to either the sweet or savory base decreased the woody/pine attributes of the flavoring. The fruity characteristics of fraction C only came out in the sweet base where it was described as being tropical, circus peanut and banana. Otherwise, hop fraction C had more woody, pine, citrus, herbal and soapy characteristics. Fraction D was higher in plastic, chemical off notes in distilled water, but also had some floral characteristics. Addition of the sweet base substantially increased the fruity and citrus characteristics of fraction D. Hop fraction E was described as being skunky, fermented, cabbagelike, musty, floral, piney and beany by the panel. The addition of fraction E to the sweet base significantly increased the citrus, lime character of this flavoring.

Discussion of Analytical Results

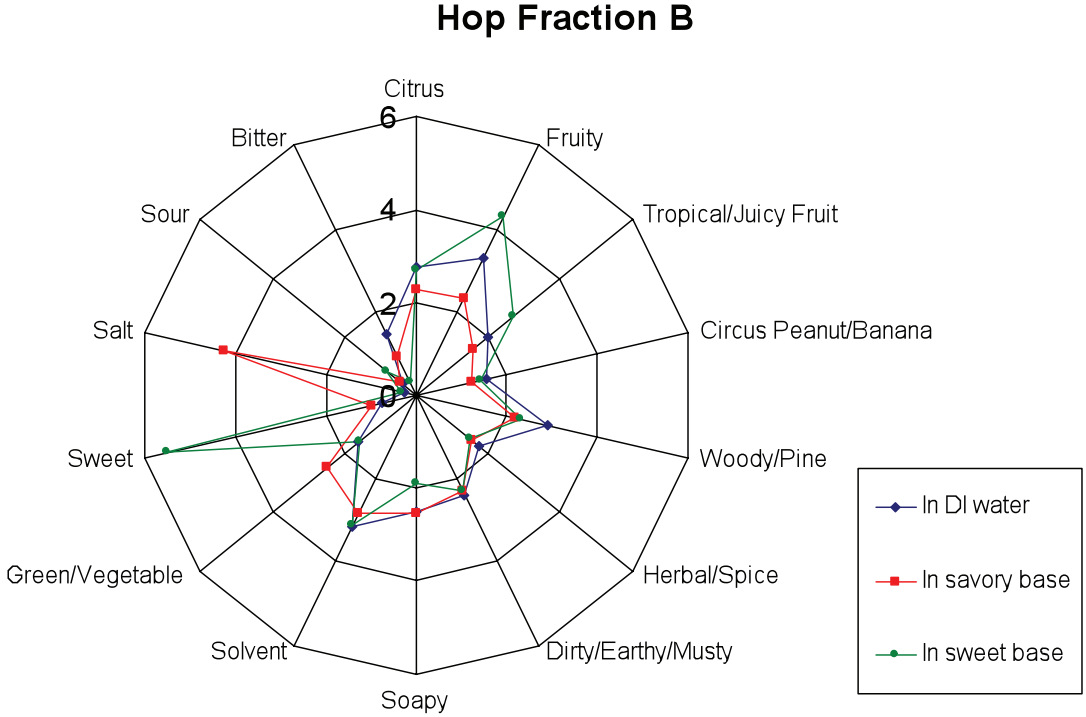
F-7 shows the GC/MS chromatogram of hop oil fraction A, with peak area % listed in **T-1**. It has two large peaks of jasmolactone (creamy, coconut) and dihydrocarvone (herbaceous, spearmintlike). It also has an interesting mix

Hop fraction	Flavor	Control (without hops)	With hops
C	Orange	**T-6.3** • Thin, weak • Intense orange, soda pop flavor • Orange, sweet, fake • Orange	**T-6.4** • Juicer, more natural, acidic • Reduced artificial candylike sweetness, subtle improvement • Greener, little orange flavor • More balanced, not as fake/synthetic • Orange, berrylike
D	Parmesan cheese	**T-7.1** • Parmesan, fatty • Cheese, aromatic, salty, sweaty feet, slight metallic • Cheese rind, aged flavor, salty, fatty • Blue cheese, fatty	**T-7.2** • Aged, brown notes • Prime rib, marinated • Less aroma, salty, cheesy, less off notes, slightly fruity • Stronger flavor cheese rind, saltier • Blue cheese, fruity
D	Melon	**T-7.3** • Fatty, melon • Plastic aroma, sweet, fruity, astringent • Papery, cucumber, sweet, melon, astringent • Green, sweet, melon, sulfur • Sweet, green, viney, cucumber, artificial flavor	**T-7.4** • Fattier, more like rind, more depth • Viney aroma, green melon, creamy, less astringency • Added citrus character, well blended • Same flavors, not as strong, more balanced, no sulfur • Green, more balanced, natural flavor
E	Beef frankfurter	**T-8.1** • Meaty, brown • Salty, waxy, plastic, savory • Meaty, brown, beefy • Salty, savory, meaty • Salty, meaty	**T-8.2** • Hot dog, brings out spices • Strong meaty aroma, brown/roasted, salty, sulfur, herbal, more complex • Added fruity, roasted, marinated • Salty, savory, meaty, herbal, roasted notes, improvement • Bring out the meaty flavor, salty

Descriptive profile of hop oil fraction A **F-2**



Descriptive profile of hop oil fraction B **F-3**



GC/MS area % of volatile compounds detected in fraction A **T-1**

Peak	Compound	A
1	Isovaleric acid	0.3
2	Caproic acid	0.3
3	Heptanoic acid—branched	0.1
4	1-Heptyn-4-ol	0.3
5	Heptanoic acid	0.3
6	4-Methyl caprylic acid	3.2
7	Caprylic acid	5.9
8	Nonanoic acid—branched	1.0
9	3-Hepten-1-ol	2.2
10	Nonanoic acid	3.0
11	Caprylic acid—branched	1.8
12	3-Decen-1-ol	1.7
13	Capric acid	3.2
14	Dihydrocarvone	35.0
15	Jasmolactone	19.6

of even, odd, and branch-chain fatty acids. Descriptions of flavor attributes of specific flavor chemicals are from Fenaroli or Flavor Base.[1,b]

F-8–11 show the GC/MS chromatograms of fractions B–E, respectively. Volatile compounds with peak area % can be found in **T-2**. Fraction B is characterized by high myrcene content (>70%, woody, citrus), while fraction C contains no myrcene, but has mostly sesquiterpenes, including caryophyllene (22%, woody, clove) and humulene (34%, woody, balsamic). Fraction D comprises several ethyl esters, while fraction E is high in linalool (13%, floral, citrus) and methyl esters.

[b]*www.leffingwell.com*

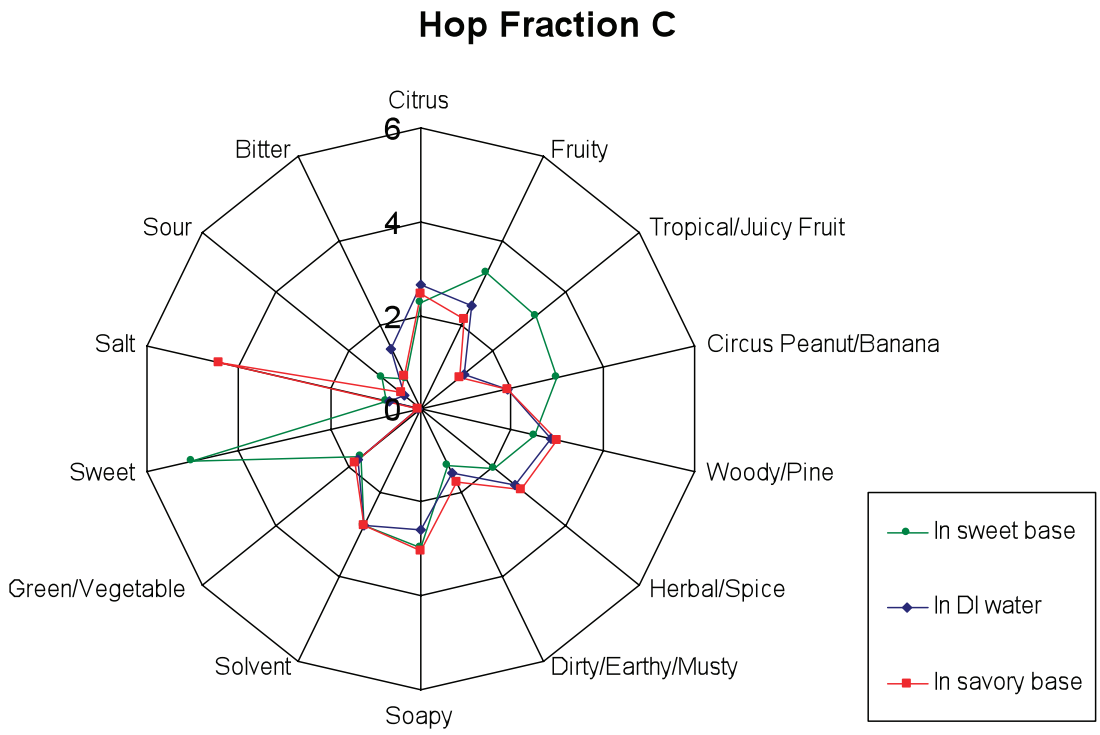
Bench Sensory Results

The authors tasted the hop oil fractions in water and described the flavor. Then they tasted the fractions in a savory base and a sweet base, and gave possible flavor applications for those fractions. **T-3** lists the author's observations after tasting the fractions. The authors comprised one flavor chemist, one hops scientist, one sensory scientist and two analytical chemists.

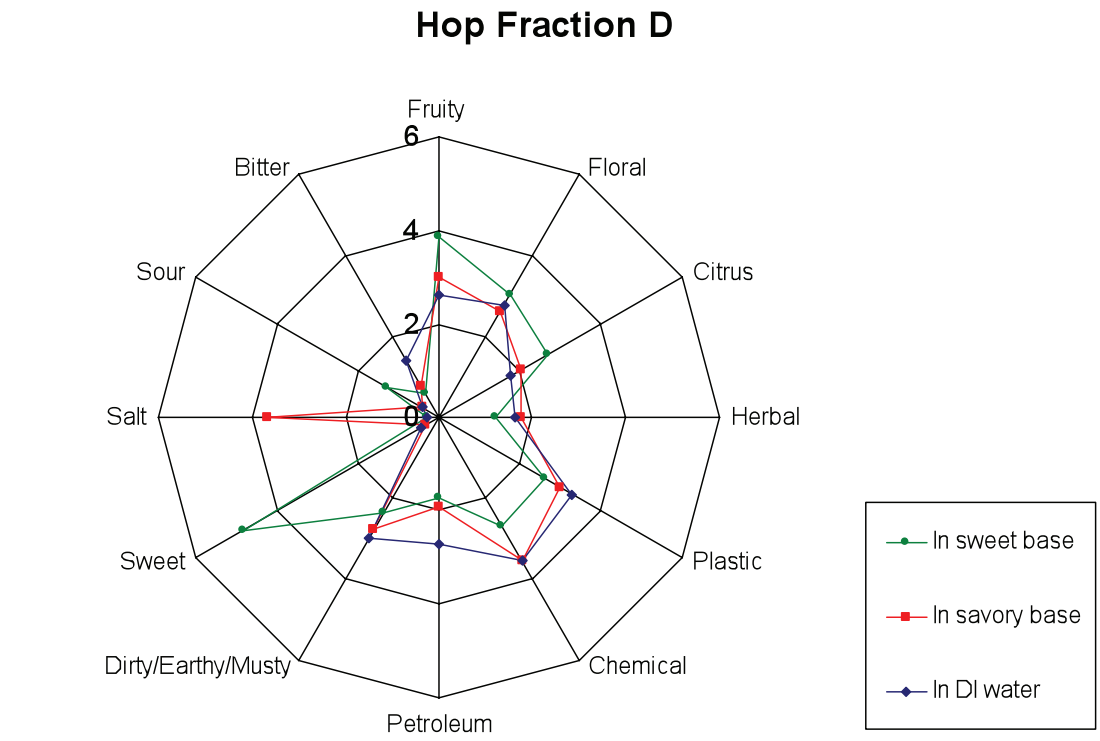
Based on the tasting notes from **T-3** and the analytical results, the flavor chemist created some simple flavors to test the effect of the addition of hop oil fractions. The flavors were tasted in an appropriate base by the authors, both with and without a selected hop oil fraction. The authors' comments are listed in the sidebar (see **Flavors With and Without Hop Oil**).

An intentionally simple coconut formula **T-4.1** is described as "sweet, waxy, and coconut" by the authors when tasted in the sweet base. When hop oil fraction A was added to the formula (**T-4.2**), the flavor became woodier and with a considerably deeper and more natural coconut flavor profile. As seen in the GC/MS analysis, hop oil fraction A contained jasmolactone, which complemented

Descriptive profile of hop oil fraction C **F-4**



Descriptive profile of hop oil fraction D **F-5**



the flavor with its creamy and coconutlike profile. The mid-chain fatty acids also helped to make the flavor more complex and natural. The description sensory profiles of the hop fraction (**F-2; sidebar**) observed the fatty waxy notes, but the citrus and fruity notes noted in the sweet base were not observed by the authors when tasting flavor **T-4.2**.

T-5 lists two flavors, a sweet raspberry flavor (**T-5.1**) and a savory roast garlic flavor (**T-5.3**). The raspberry flavor tasted sweet, berry-like, and somewhat unnatural. The addition of hop oil fraction B increased the green notes and made the flavor (**T-5.2**) more rounded and authentic tasting. The flavor **T-5.3** was described as roasted garlic, but adding the hop oil reduced the garlic oil note and increased the brown, roasted notes. Hop oil fraction B contained a considerable amount of myrcene (see **T-2**). The flavor profile (**F-4; sidebar**) demonstrated fruity, citrus notes in sweet base and woody, herbal notes when tasted in savory base. It seemed to add seedy, woody notes to the raspberry flavor, while increasing the cooked savory notes in the roasted garlic flavor.

T-6 shows two sweet applications using hop oil fraction C. This fraction is primarily characterized by the woody compounds caryophyllene and humulene (see **T-2**). The sensory profile (**F-3**) highlighted these notes in the savory base, yet showed more fruity, citrus, and tropical notes in the sweet base. The root beer flavor **T-6.1** is very sweet and one-dimensional from the methyl salicylate. Adding the hop oil (**T-6.2**) reduced the sweetness from the methyl salicylate and vanillin, increased the woody notes and made it a more natural tasting beverage. The orange (**T-6.3**) moved away from a "fake" orange like inexpensive sodas to a more natural, balanced flavor (**T-6.4**).

Hop oil fraction D contained esters (**T-2**) and, not surprisingly, exhibited fruity flavors (**F-5**). Formulas with hop oil fraction D are shown in **T-7**. A simple Parmesan cheese flavor **T-7.1** was described as fatty, aged cheese. When the hop oil fraction was added (**T-7.2**), the flavor changed subtly with an increase of fruitiness and brown, almost meaty notes. The melon flavor (**T-7.3**) was modified by the hop oil (**T-7.4**), exhibiting more balanced, and natural profile.

The final flavors used hop oil fraction E. This fraction is characterized by a high linalool content (**T-2**) and a flavor profile of citrus and other descriptors that may be due to sulfur compounds (**F-6**). The flavor **T-8.1** is a meaty flavor with a commercially obtained hot dog oleoresin seasoning, which is a blend of several spice extracts including black pepper, nutmeg and coriander. The flavor with hop oil added (**T-8.2**) had a remarkable effect, increasing meaty, savory, and roasted notes and bringing out the spice notes from the seasoning.

GC/MS area % of volatile compounds detected in fractions B-E **T-2**

Peak	Compound	B	C	D	E
1	Sabinene	3.2			
2	Myrcene	72.6			
3	Isoamyl butyrate	3.6			
4	Limonene	7.4		17.6	
5	Unknown methyl ester				4.8
6	Perillene				4.5
7	Linalool	1.2			12.7
8	Ethyl heptanoate			0.9	
9	Unknown compound ($C_{10}H_{18}O$)				4.3
10	Methyl octanoate				2.9
11	Ethyl ester			3.4	
12	Methyl ester				3.0
13	Methyl ester				7.7
14	Ethyl octanoate			2.7	
15	Methyl ester				1.4
16	Methyl nonanoate				2.3
17	Unknown compound			2.6	
18	Unknown compound ($C_{12}H_{24}O$)				1.9
19	Ethyl ester			2.0	
20	Methyl ester				3.0
21	Unknown compound			2.6	
22	Methyl ester		1.5		14.8
23	Unknown compound				3.6
24	Ethyl ester			2.4	
25	Ylangene		0.8		2.8
26	Copaene		2.4		6.6
27	Ethyl-(4E)-decenoate			18.7	
28	Unknown compound			8.6	
29	Ethyl decanoate			2.9	
30	Caryophyllene		22.4	0.9	
31	Humulene		34.2	3.0	
32	γ-Muurolene		3.3		
33	β-Selinene		2.4		
34	α-Selinene		3.4		
35	γ-Cadinene		2.9		
36	δ-Cadinene		4.9		
37	Unknown compound ($C_{15}H_{24}$)		1.8		
38	Unknown compound ($C_{15}H_{24}$)		1.6		
39	Unknown compound			1.8	
40	Unknown compound			1.4	
41	Unknown compound			4.7	

Tasting notes of hop oil fractions by authors **T-3**

Product Code	Water Descriptions	Savory Applications	Sweet Applications
Fraction A	• Waxy, woody • Waxy, cheesy, caprylic • Fatty, musky, old, woody • Plastic, sulfur • Paper, plastic, woody	• Meat, roasted • Soup stock • Onion and garlic • Roast chicken	• Coconut • Melon • Apple • Tropical • Coconut
Fraction B	• Floral, fruity • Mango, piney, scotch tape, plastic, cologne, woody • Sweet, fruity, chemical, bubble gum • Fruity, berry, slightly sour, fruity, Juicy Fruit, bubblegum	• Meat/marinade • Delivers sweetness to a roasted note • Onion and garlic • Chip dip • Roast garlic or beef	• Candy • Bubblegum • Fruit juice • Jam • Jellies • Raspberry • Juicy Fruit
Fraction C	• Rose, leafy • Woody, resinous, floral, cologne • Harsh, oily • Citrus, green/viney, fruity • Spicy, pungent, floral, green	• Mushroom • Tobacco • Mushroom	• Cologne • Candy • Gums • Chinese gum • Mint combo • Orange or mint
Fraction D	• Fruity, ester, floral • Fruity, ester, sweet, brandy, soapy, waxy • Fatty acids, greasy • Fatty, green • Berry, plastic, woody	• Waxy cheese • Goat cheese • Wax bottle candies	• Citrus rind • Papaya • Guava • Coconut • Soapy • Melon
Fraction E	• Fatty, slightly brown • Floral, vitamin, cheesy • Fermented, isovaleric, greasy • Musty, fermented • Garbage, sulfur, fermented, cabbage	• Kimchi • Fermented foods • Fermented soy • Blue cheese • Cabbage • Chip dip • Blue cheese	• Tea

Summary and Conclusions

Hop oils, which are responsible for the hop aroma in beer, can be isolated from CO_2 extracted hops, and fractionated by vacuum distillation. This paper characterized several commercial hop oil fractions by sensory and instrumental techniques. This information was used to make a number of non-beer flavors in which the effects of small percentages of hop oils were added, and the flavor profiles compared. Overall, hop oil fractions were effective in modifying the flavors to either add more complexity and natural, rounded flavor balance, or accentuate some nuances in the flavor.

The particular characteristics of hop oil fractions can be easily modified by varying the parameters of the fractionation process. In addition, the fractions could be recombined for a particular flavor profile. Hop oil fractions are novel flavor ingredients that can make positive contributions to a wide variety of flavors.

Flavor formula with hop oil fraction A **T-4**

Coconut	T-4.1 (%)	T-4.2 (%)
Furaneol 20% PG	0.20	0.20
Acetoin	0.05	0.05
Methylthiobutyrate 5%	0.10	0.10
cis-3-Hexen-1-ol	0.05	0.05
γ-Octalactone	3.00	3.00
δ-Decalactone	1.00	1.00
Vanillin	0.40	0.40
Hop oil fraction A	0.00	0.25
Ethyl alcohol	95.20	94.95
	100.00	**100.00**

Tasted at 0.01% in sweet base.

Flavor formulas with hop oil fraction B — T-5

Raspberry	**T-5.1 (%)**	**T-5.2 (%)**
Raspberry ketone	10.00	10.00
α-Ionone	1.00	1.00
cis-3-Hexen-1-ol	5.00	5.00
Benzyl acetate	1.00	1.00
Damascenone 1%	1.00	1.00
β-Ionone	0.20	0.20
Vanillin	5.00	5.00
Hop oil fraction B	0.00	0.20
Ethanol	76.80	76.60
	100.00	**100.00**

Tasted at 0.01% in sweet base.

Roast garlic	**T-5.3 (%)**	**T-5.4 (%)**
Garlic oil	0.25	0.25
Furfuryl thioacetate 0.1%	0.05	0.05
Furfural	0.20	0.20
2,3,5-Trimethylpyrazine 1%	0.10	0.10
Hop oil fraction B	0.00	0.05
Ethyl alcohol	95.40	95.35
	100.00	**100.00**

Tasted at 0.01% in savory base.

Flavor formulas with hop oil fraction C — T-6

Root beer	**T-6.1 (%)**	**T-6.2 (%)**
Methyl salicylate	9.00	9.00
Anise oil	0.50	0.50
Lemon oil	0.30	0.30
Oil of coriander	0.10	0.10
Vanillin	2.00	2.00
Hop oil fraction C	0.00	0.08
Ethyl alcohol	88.10	88.08
	100.00	**100.00**

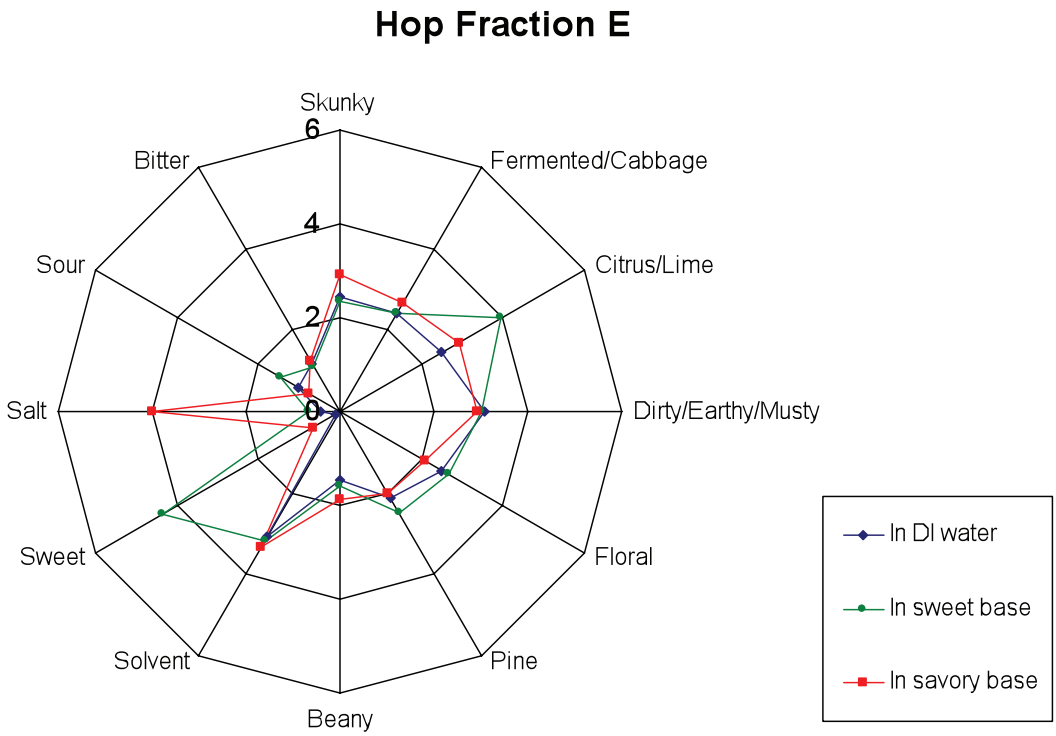
Tasted at 0.01% in a 7% sugar solution.

Orange	**T-6.3 (%)**	**T-6.4 (%)**
Orange oil, cold pressed	10.00	10.00
Decanal	0.05	5.00
Octanal	0.05	5.00
Ethyl butyrate	1.00	1.00
Tropathiane 0.01%	0.10	0.10
Ethyl acetate	1.00	1.00
Hop oil fraction C	0.00	0.03
Ethyl alcohol	87.80	87.77
	100.00	**100.00**

Tasted at 0.01% in sweet base.

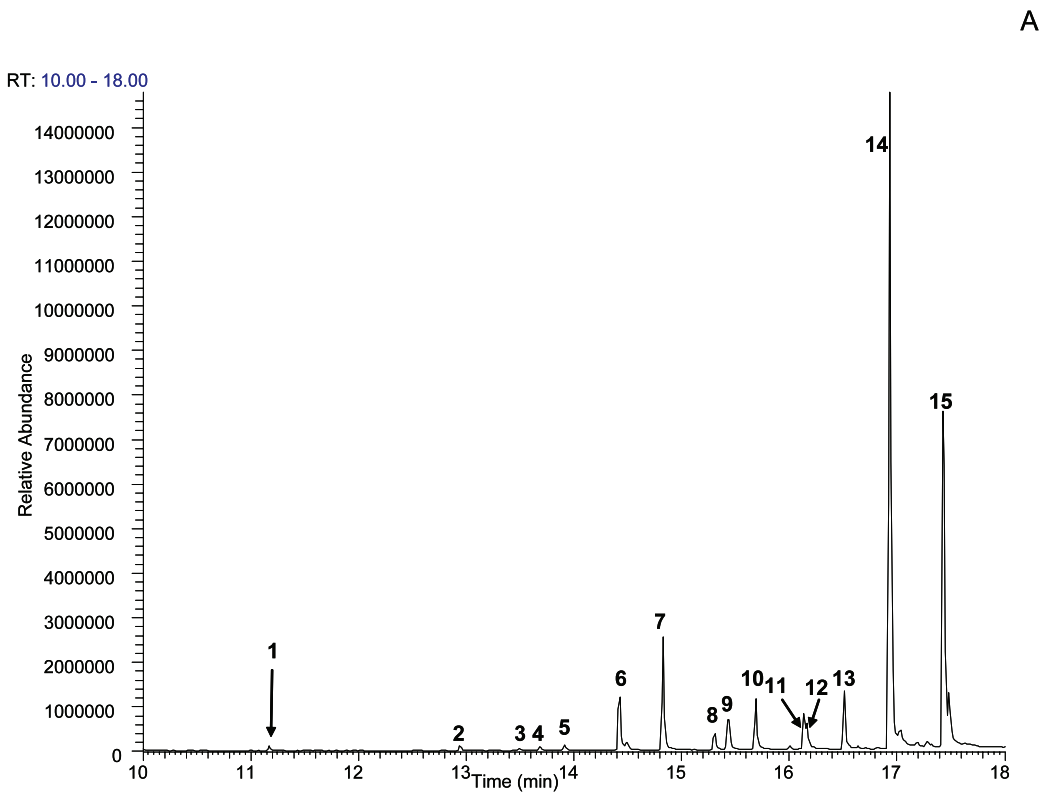
Descriptive profile of hop oil fraction E

F-6



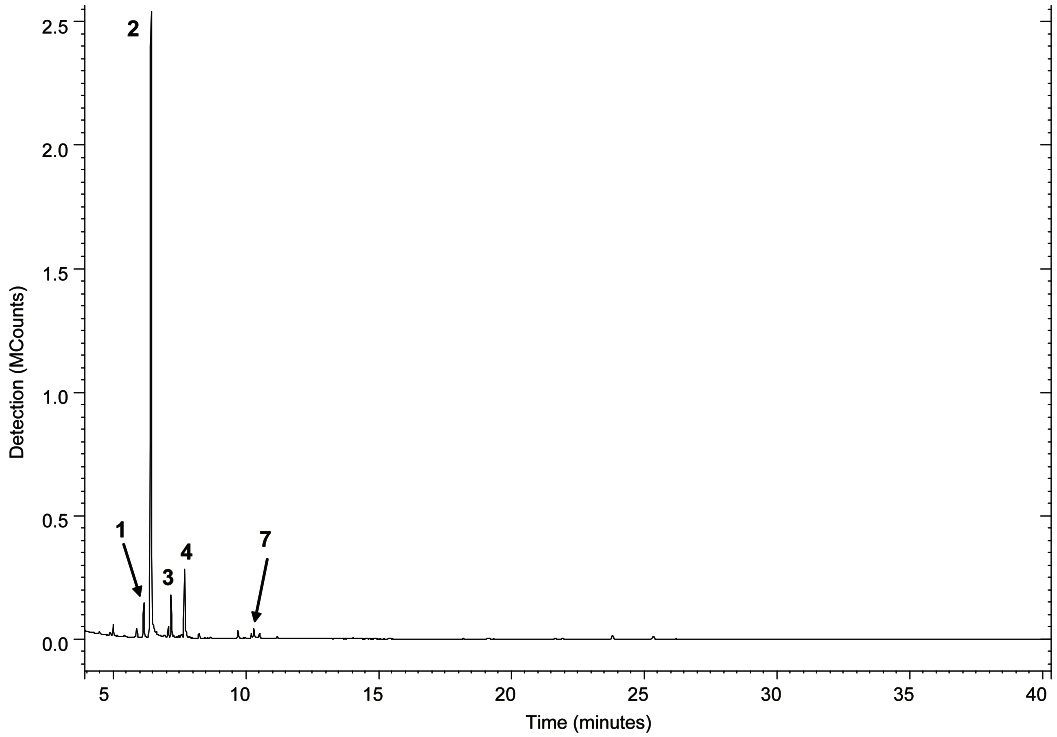
GC/MS chromatogram of hop oil fraction A

F-7



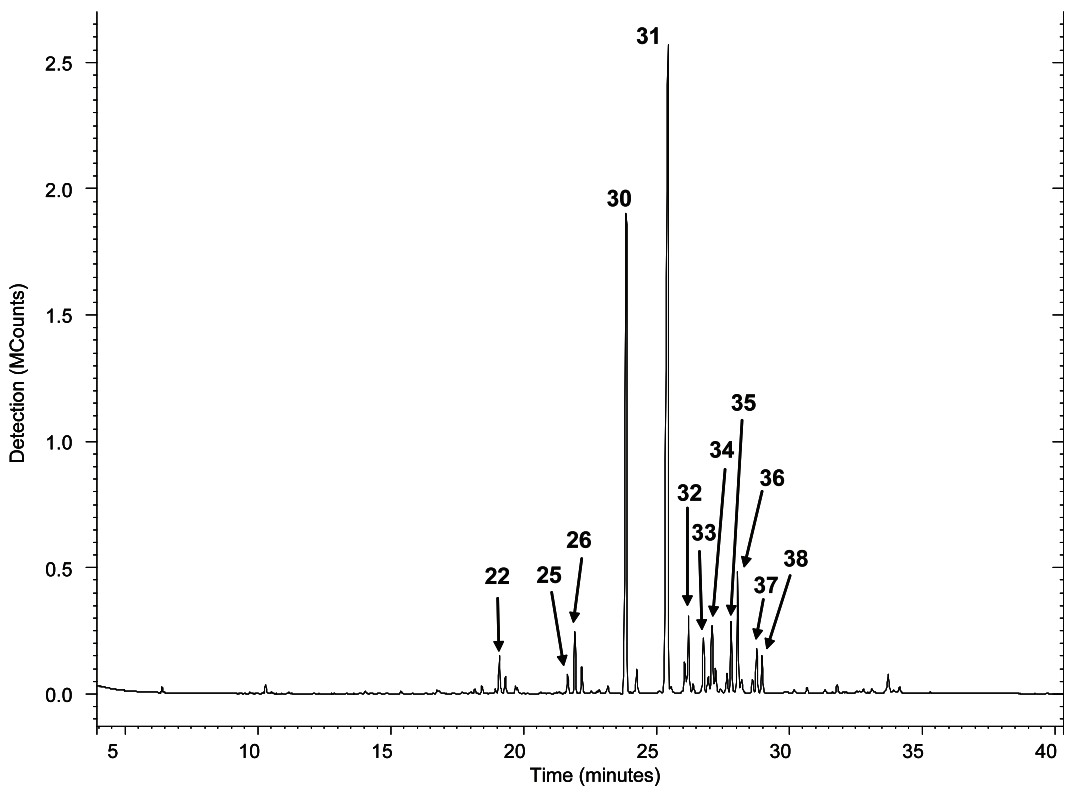
GC/MS chromatogram of hop oil fraction B

F-8



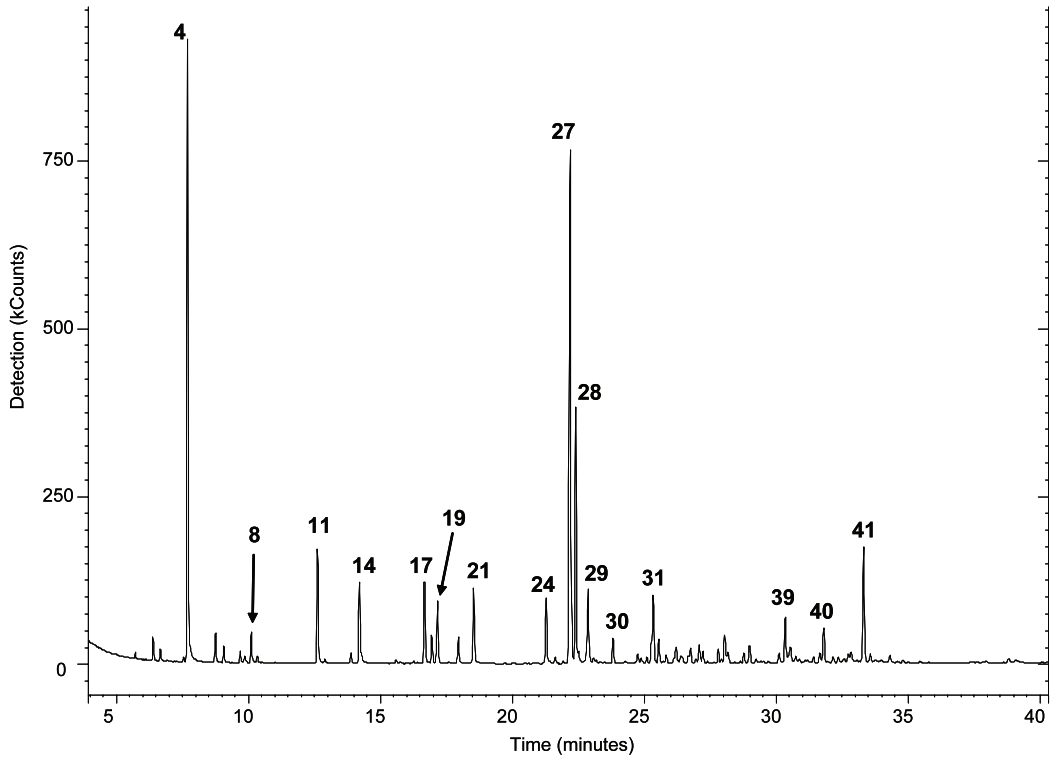
GC/MS chromatogram of hop oil fraction C

F-9



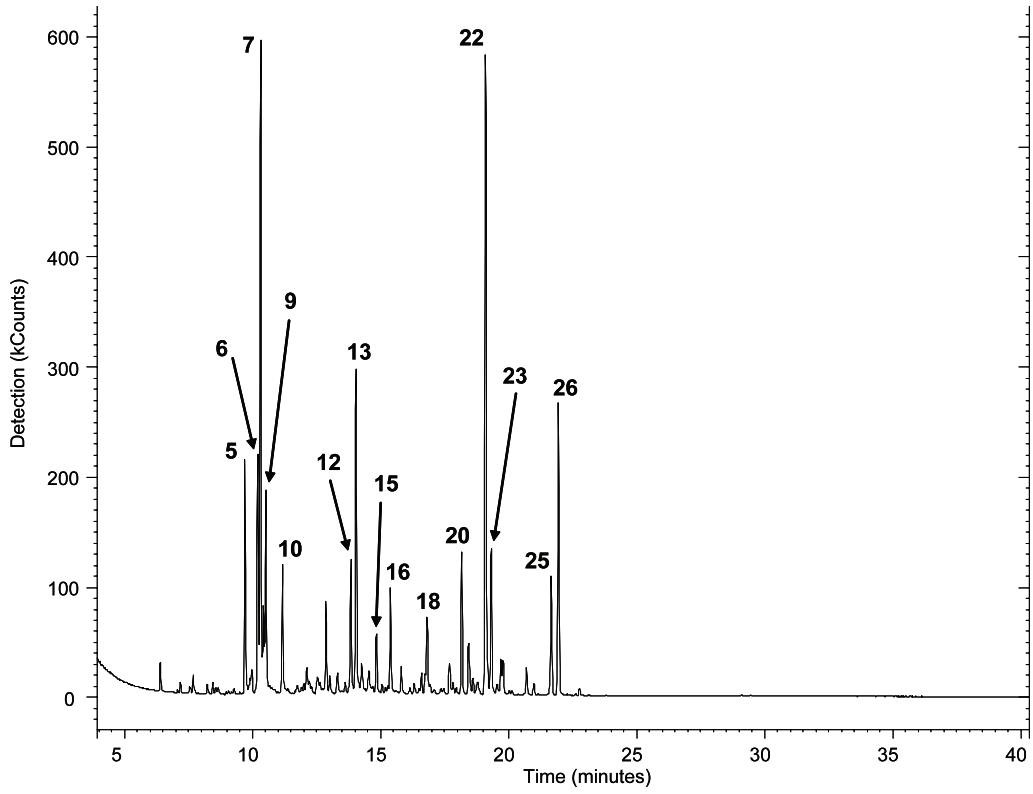
GC/MS chromatogram of hop oil fraction D

F-10



GC/MS chromatogram of hop oil fraction E

F-11



Flavor formulas with hop oil fraction D — T-7

Parmesan cheese	T-7.1 (%)	T-7.2 (%)
Butyric acid	1.00	9.00
Caproic acid	2.00	0.50
Caprylic acid	2.00	0.30
Capric acid	1.50	0.10
3-Methylpentanoic acid	0.50	2.00
Methional 1% in PG	0.10	0.08
Lactic acid	5.00	5.00
Furaneol 20% in PG	0.40	0.40
Hop oil fraction D	0.00	0.50
Ethyl alcohol	87.50	87.00
	100.00	**100.00**

Tasted at 0.01% in savory base.

Melon	T-7.3 (%)	T-7.4 (%)
Melonal	2.00	10.00
trans-2,*cis*-6-Nonadienal 1%	1.00	5.00
Strawberry furanone 20%	1.00	5.00
trans-2,*cis*-6-Nonadienol 1%	0.25	1.00
trans-2-Nonenal 1%	1.00	0.10
Hop oil fraction D	0.00	0.10
Ethyl alcohol	94.75	94.65
	100.00	**100.00**

Tasted at 0.01% in sweet base.

Flavor formula with hop oil fraction E — T-8

Beef frank	T-8.1 (%)	T-8.2 (%)
2-Methyl-3-furanethiol 5%	0.05	0.05
Hot dog spice blend	2.50	2.50
Lactic acid	2.00	2.00
Furaneol 20%	2.00	2.00
Oleoresin fenugreek	8.00	8.00
Acetyl propionyl	0.05	0.05
Hop oil fraction E	0.00	0.05
Propylene glycol	85.40	85.35
	100.00	**100.00**

Tasted at 0.01% in savory base.

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References

1 GA Burdock, *Fenaroli's Handbook of Flavor Ingredients, Fifth Ed.* CRC Press, Boca Raton (2004)