Cooking With Alliums

Maillard reactions with different forms of onion and garlic extracts.

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Flavor chemists often use Maillard reaction technology to make savory flavors. Realistic meat and processed flavors can be made using this technology by simulating the ingredients and conditions of authentic cooking. Typically, this reaction requires an amino acid source, such as a defined amino acid or a protein hydrozylate, and reducing sugar. In meat flavors, sulfur from cysteine is often employed.

In the reactions in this paper, cysteine is supplemented with the sulfur-containing extracts of onion (*Allium cepa*) and garlic (*Allium sativum*), common ingredients in savory cooking. These extracts are available in three forms: essential oil, powder, and juice. This paper examines how the three types of extracts perform in some model Maillard flavor reactions.

Materials and Methods

Onion and garlic oils were standardized product codes provided by Kalsec. Onion, garlic and yeast extract powders were obtained from commercial sources. The onion and garlic juices were also from commercial sources and contained salt as preservative for the high moisture products.

Reactions

The reactions were formulated by the flavor chemist, and the reaction performed in a Parr reactor (Moline, IL). Formulae of the reactions with percent by weight ingredients are shown in **T-1**, **T-2** and **T-3**. Attempts were made to keep the moisture and sodium levels equivalent between reactions of the same flavor profile using the different extracts while maintaining approximately equal sensory intensity. A control for each flavor profile with no allium extract was also made to aid in the analytical analysis. After the reactions, the products were submitted for analytical and sensory analyses.

Beef reaction with onion extract: The formulae for the beef-type flavor reaction are depicted in **T-1**. Cysteine provides sulfur for most meat-type reactions, with some methionine added as well. Arginine is used in many beef-type flavors, and glutamic acid.[1] Rhamnose creates furaneol, a key contributor to beef flavor.[2] Xylose is a highly reactive pentose. The strategy is to form complicated heterocyclic compounds, such as the characterizing 2-methyl-3-furanthiol. Lactic acid adjusts the pH of the reaction, and also is found in meat. Glycerine is a polar carrier, and also controls the water activity. The three onion extracts were added to be approximately the same onion strength in the final product. Water and salt contents were manipulated to be similar between the four reactions. The canola oil was added as a diluent in order to accurately weigh the onion oil. The reactions (300 g each batch) were reacted for 150 min at 105ºC in a closed vessel.

Chicken reaction with garlic extract: The chicken reactions with garlic extracts are depicted in **T-2**. The strategy for these reactions is to make simpler sulfur compounds. Therefore, the reaction time is shortened and a less reactive hexose (fructose) is used as a reducing sugar. Chicken is more sulfury than beef, so more cysteine was added.[1] Arginine was removed. Ascorbic acid and cystiene react to form a chickenlike flavor.[3] Chicken fat is highly unsaturated, and provides much of the characteristic flavor of chicken. Since this is a vegetarian reaction, safflower

T-1. Beef-type flavor reaction with onion extract

Ingredient	1C Control (%)	1J With Juice (%)	1P With Powder (%)	1O With Oil (%)
L-Arginine	1.00	1.00	1.00	1.00
L-Cysteine	1.00	1.00	1.00	1.00
L-Methionine	0.10	0.10	0.10	0.10
L-Glutamic acid	4.00	4.00	4.00	4.00
L-Rhamnose	1.00	1.00	1.00	1.00
D-Xylose	2.00	2.00	2.00	2.00
Water	12.66	0.00	12.45	12.66
Salt	1.02	0.00	1.01	1.02
Glycerine	73.21	71.90	68.44	73.22
Canola oil	0.99	0.99	0.99	0.99
Lactic acid 88%	3.00	3.00	3.00	3.00
Onion oil	0.00	0.00	0.00	0.01
Onion powder	0.00	0.00	5.00	0.00
Onion juice	0.00	15.00	0.00	0.00
Totals	**100.00**	**100.00**	**100.00**	**100.00**

T-2. Chicken-type flavor reaction with garlic extract

Ingredient	2C Control (%)	2J With Juice (%)	2P With Powder (%)	2O With Oil (%)
L-Arginine	1.00	1.00	1.00	1.00
L-Cysteine	3.00	3.00	3.00	3.00
L-Methionine	0.10	0.10	0.10	0.10
L-Glutamic acid	3.00	3.00	3.00	3.00
L-Rhamnose	0.25	0.25	0.25	0.25
D-Fructose	3.00	3.00	3.00	3.00
Ascorbic acid	1.00	1.00	1.00	1.00
Water	9.00	0.00	8.73	9.00
Salt	1.48	0.00	1.47	1.48
Glycerine	74.17	69.75	70.33	74.15
Safflower oil	2.00	2.00	2.00	2.00
Lactic acid 88%	3.00	3.00	3.00	3.00
Garlic oil	0.00	0.00	0.00	0.02
Garlic powder	0.00	0.00	4.11	0.00
Garlic juice	0.00	15.00	0.00	0.00
Totals	**100.00**	**100.00**	**100.00**	**100.00**

T-3. Vegetable broth flavor reaction with onion and garlic extracts

Ingredient	3C Control (%)	3J With Juice (%)	3P With Powder (%)	3O With Oil (%)
Oleoresin carrot	5.00	5.00	5.00	5.00
Oleoresin celery	5.00	5.00	5.00	5.00
Canola oil	90.00	90.00	90.00	90.00
D-Dextrose	2.50	2.50	2.50	2.50
Autolyzed yeast	2.50	2.50	2.50	2.50
Water	21.66	0.00	21.19	21.66
Salt	2.50	0.00	2.48	2.50
Lactic acid 88%	3.00	3.00	3.00	3.00
Onion oil	0.00	0.00	0.00	0.01
Onion powder	0.00	0.00	5.00	0.00
Onion juice	0.00	15.00	0.00	0.00
Garlic oil	0.00	0.00	0.00	0.02
Garlic powder	0.00	0.00	4.11	0.00
Garlic juice	0.00	15.00	0.00	0.00
Totals (oils only)	**100.00**	**100.00**	**100.00**	**100.00**

T-4. GC Temperature gradient

Temperature (°C)	Rate (°C/min)	Hold time (min)
40	-	5
140	3	-
240	10	4

was added instead. Reaction conditions were 105ºC for 90 minutes. The flavor was too acidic after reacting, so the pH was adjusted to 5.5–6.0 after the reaction to improve palatability.

Vegetable broth flavor reaction with onion and garlic extracts: The third reaction, a vegetable broth reaction, is considerably different, **T-3**. Canola oil is the carrier. After the reaction, the oil is decanted from the aqueous residue, and the oil filtered via suction filtration through filter paper. The flavor is reminiscent of mirepoix, mainly flavored by celery and carrot oleoresins. The Maillard reactants for the control sample were yeast extract and dextrose. The only sulfur sources are onion and garlic extracts. Formulae were made to 100% oil, and reacted for 121ºC for 60 min.

Analytical

Reaction flavors were sampled by headspace solid phase microextraction (SPME), using a 50/30 µm DVB/Carboxen/PDMS SPME fiber (Supelco, Bellefonte, PA). Volatile analysis was done by gas chromatography mass spectrometry (GC/MS), using a Varian 3800 GC and Varian Saturn 2000 MS (Palo Alto, CA). Samples were analyzed with no dilution or addition of any solvent, with 0.1 min adsorption at 25ºC and 3 min desorption in the GC injector set at 240°C. GC temperature gradient is summarized in **T-4**. Helium was used as carrier gas, at a constant flow rate of 1 mL/min. A Supelco fused silica SLB-5ms column (30 m x 0.25 mm ID; 0.25 µm film thickness) was used for separation of the volatile compounds. MS detection range was 30–300 m/z, with a scan rate of 0.7 sec/scan. Tentative peak identification was done using several inline libraries, including NIST98, and Adams.[4]

Sensory

A basic savory base system consisting of 3 g salt plus 0.5 g monosodium glutamate (MSG) for every 1,000 g of water was used to test the reaction flavors with differing forms of onion and garlic extracts. Samples were prepared 1–2 hours before sensory evaluation and were served at room temperature. Descriptive panelists (n=12–15) trained using a modified spectrum methodology on a 0–15 universal scale evaluated the beef reaction with onion sources, the chicken reaction with garlic sources and the vegetable broth reaction with garlic and onion sources over a series of panel sessions. Panelists evaluated the blindly coded 2-ounce samples individually, discussed attributes as a group and rated attributes individually. Panelists were allowed to cleanse their palates with distilled water or crackers, as needed.

Statistics were run using Compusense software, sample P-values were calculated using analysis of variance (2-way). Typically, $P \leq 0.05$ is considered statistically significant, while 0.05 < $P \leq 0.10$ is considered borderline statistically significant.

Results and Discussion

F-1 and **F-2** show descriptive sensory profiles of the beef flavor reactions with added onion essential oil, juice and powder. The beef reaction formulated with onion oil was described as having significantly more fermented aroma ($P < 0.05$) and flavor ($P = 0.02$) characteristics. Panelists found the juice and powder formulations to be similar in profile.

F-3 shows the GC/MS chromatograms of beef type flavor reactions with onion extracts.

F-4 and **F-5** depict descriptive sensory profiles of the chicken flavor reactions with added garlic essential oil, juice and powder. Panelists found the three formulations to be similar in profile. The reactions containing garlic oil were slightly higher in fermented and green/herbal characteristics. Brown aroma and flavor attributes were associated more strongly in the powder reactions but not to a significant degree.

GC/MS chromatograms of chicken reaction flavors with garlic extracts are shown in **F-6**.

F-7 and **F-8** show descriptive sensory profiles of the vegetable broth flavor reactions with added onion and garlic essential oil, juice and powder. The onion and garlic oil, juice and powder inputs had a greater impact on the sensory profile than the previous reactions. Onion and garlic powder expressed the strongest with significantly more overall aroma ($P < 0.01$), onion/garlic aroma ($P < 0.01$) and flavor ($P = 0.01$) and browned aroma and flavor attributes. Panelists found the reaction formulated with onion and garlic juice to be weaker than the reaction formulated with oil.

GC/MS chromatograms of vegetable reaction flavors with garlic and onion extracts are presented in **F-9**.

Discussion

In beef, onion oil was noticeable for greater "fermented" onion flavor (**F-1** and **F-2**). It also has somewhat less meaty and brothy notes compared to the other extracts, as well as burnt and dirty notes. Otherwise, differences were minor. Juice tended to be similar to the powder. The powder, however, had greater brown aroma and flavor, probably due to the additional sugars and amino acids in the powder.

Analytical work performed on the beef reaction flavors (**F-3**) showed that 2-methyl furan, furfural, and 5-methyl furfural were the predominantly produced volatile compounds. Sample 1O was the only onion-containing reaction flavor that had some measurable levels of volatile compounds characteristic of onion, specifically methyl propyl disulfide and dipropyl disulfide.

In the chicken (**F-4** and **F-5**), garlic oil had somewhat more petroleum and fermented aromas, and less chicken aroma. The powder had more browned aroma. The juice had the least fermented and petroleum aromas, but the greatest dirty notes. It also had the least fatty flavor.

By headspace SPME GC/MS, 2-acetylfuran was the only peak that could be detected in all four chicken reaction flavors. When garlic was added as a reagent, we detected allyl mercaptan, allyl methyl sulfide, diallyl sulfide, and diallyl disulfide in the final products 2J, 2P, and 2O, with sample 2O containing the highest levels of these compounds (**F-6**).

Vegetable broth and onion and garlic powders had a much greater impact in the oil reactions than the oils or juices (see **F-7** and **F-8**). This was especially evident in the brown and

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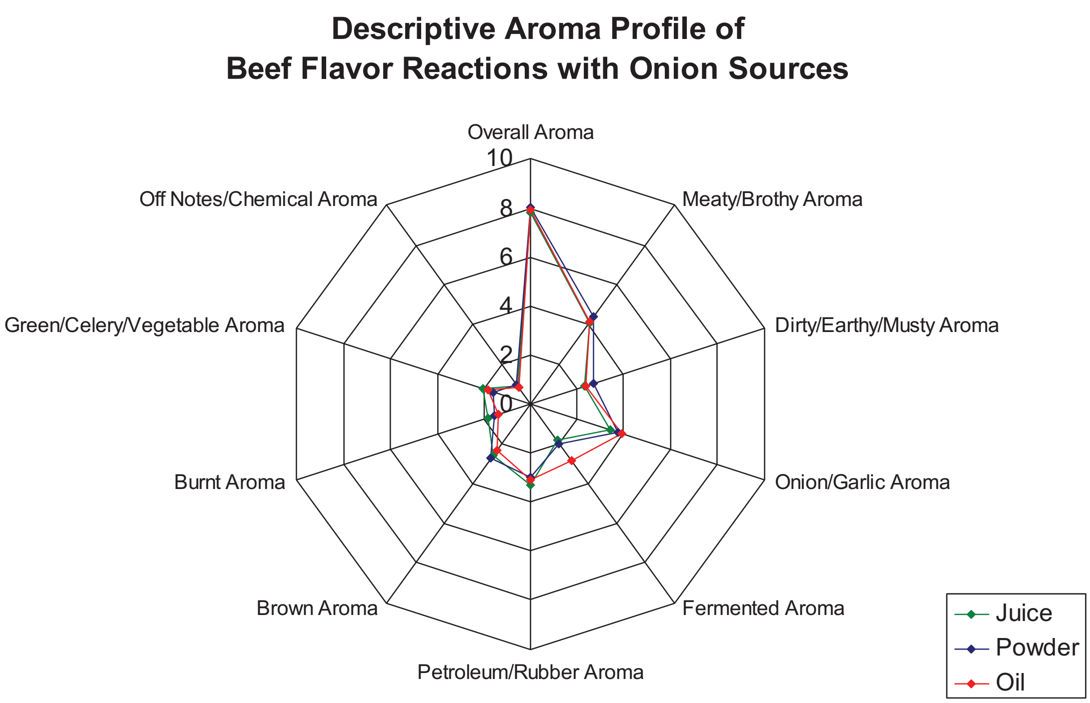
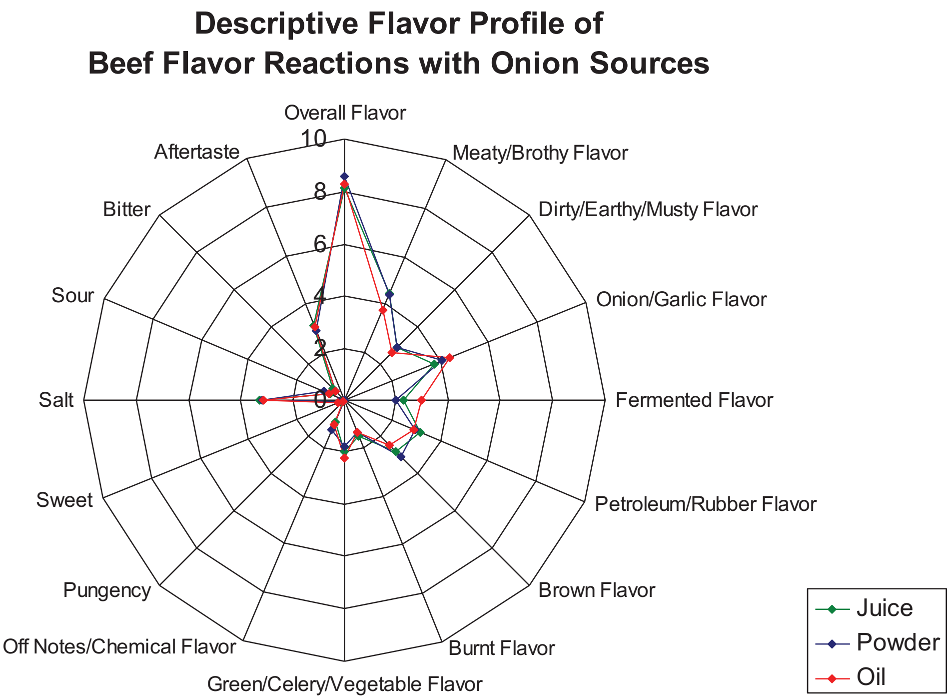
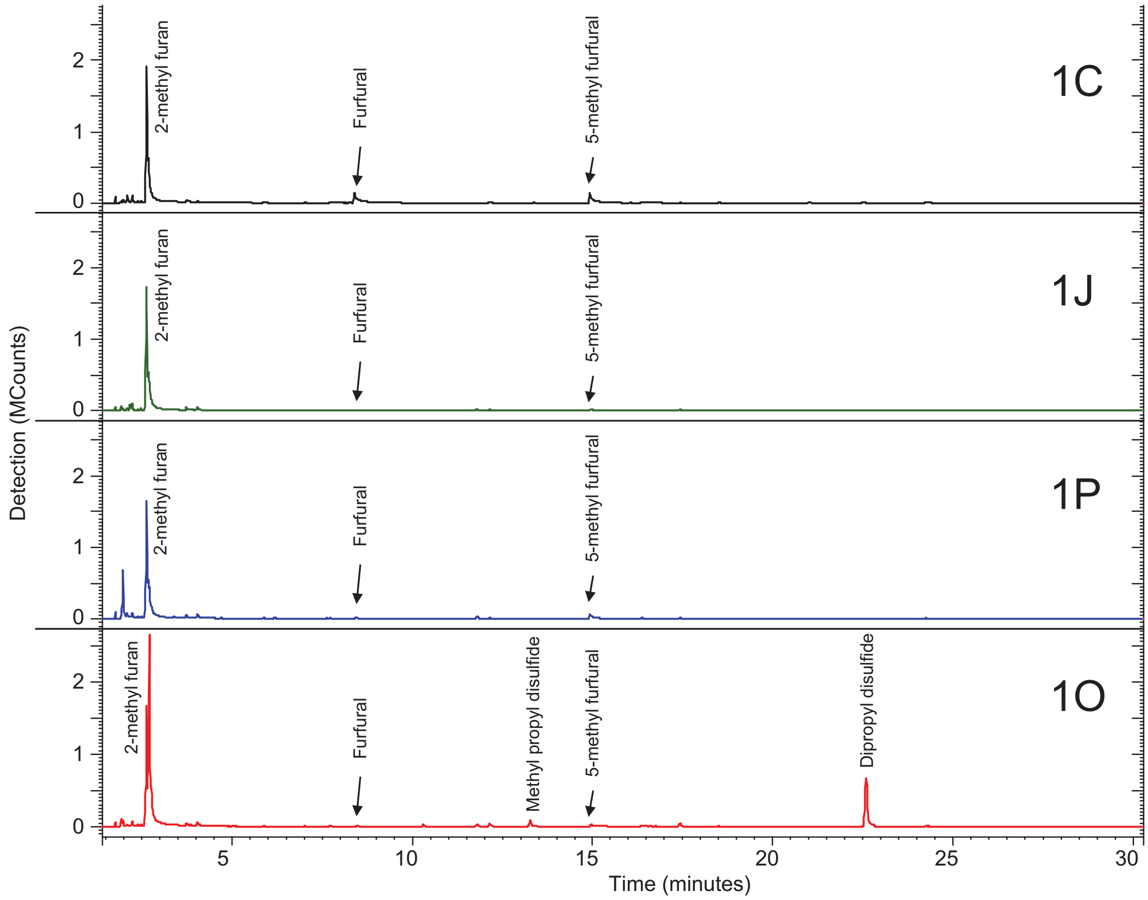
F-1. Sensory aroma profile of beef-type flavor reactions with added onion juice, onion powder or onion oil



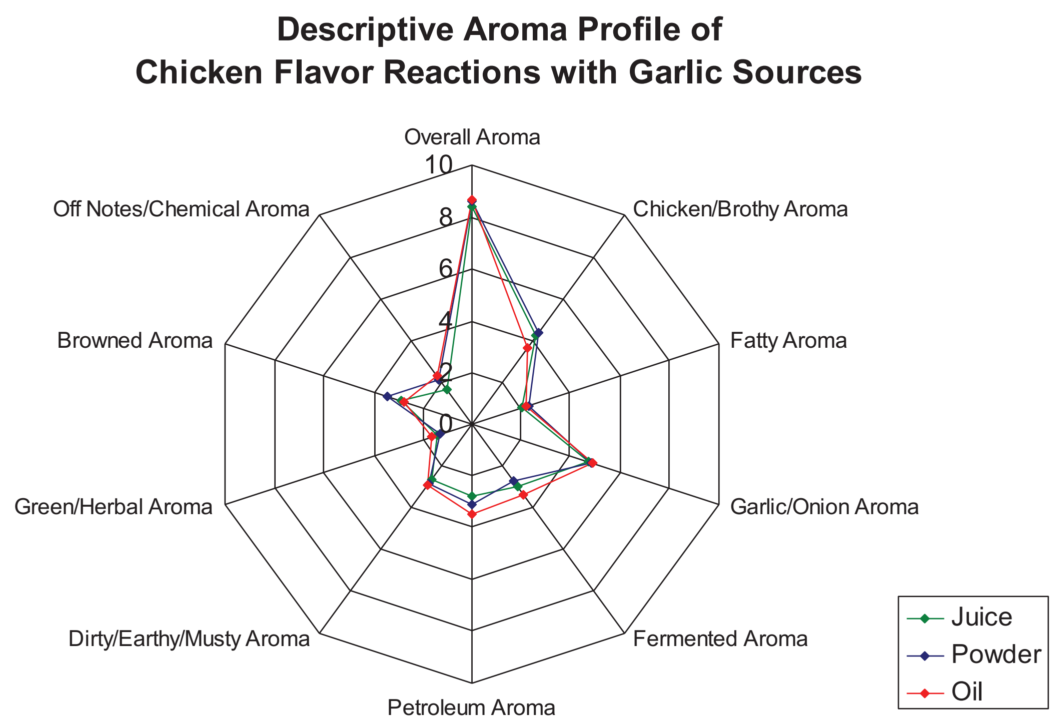
F-2. Sensory flavor profile of beef type flavor reactions with added onion juice, onion powder or onion oil



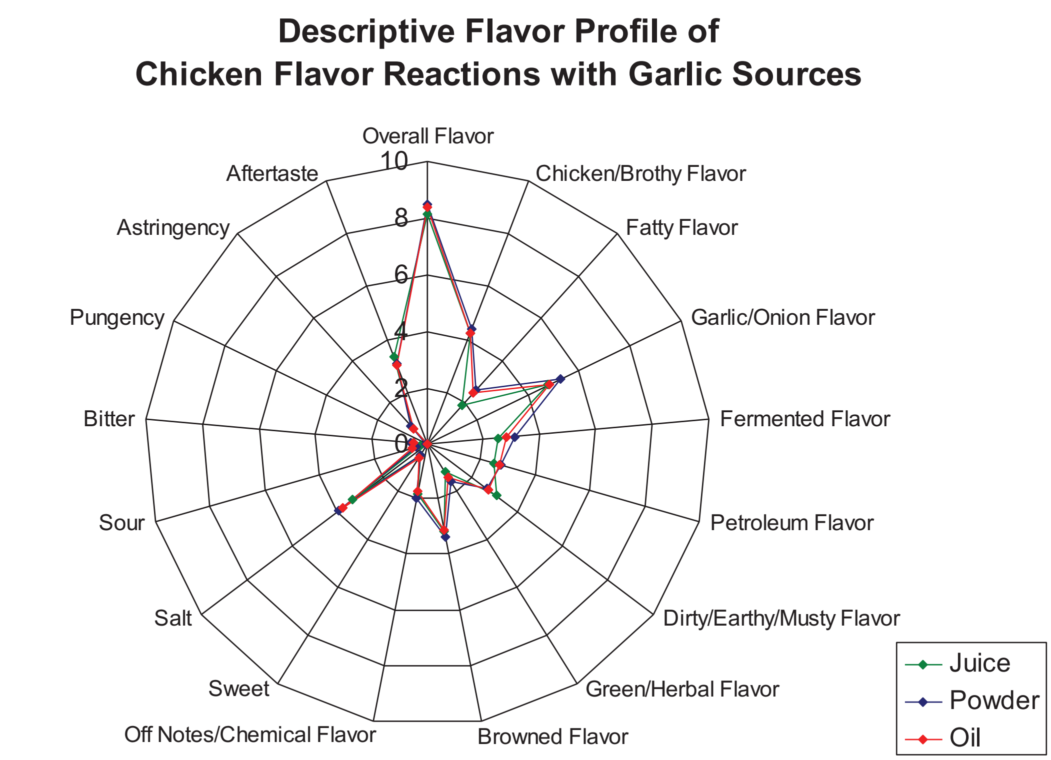
F-3. Headspace SPME GC-MS chromatograms of beef reaction flavors with no onion added (1C), or with added onion juice (1J), onion powder (1P), or onion oil (1O)



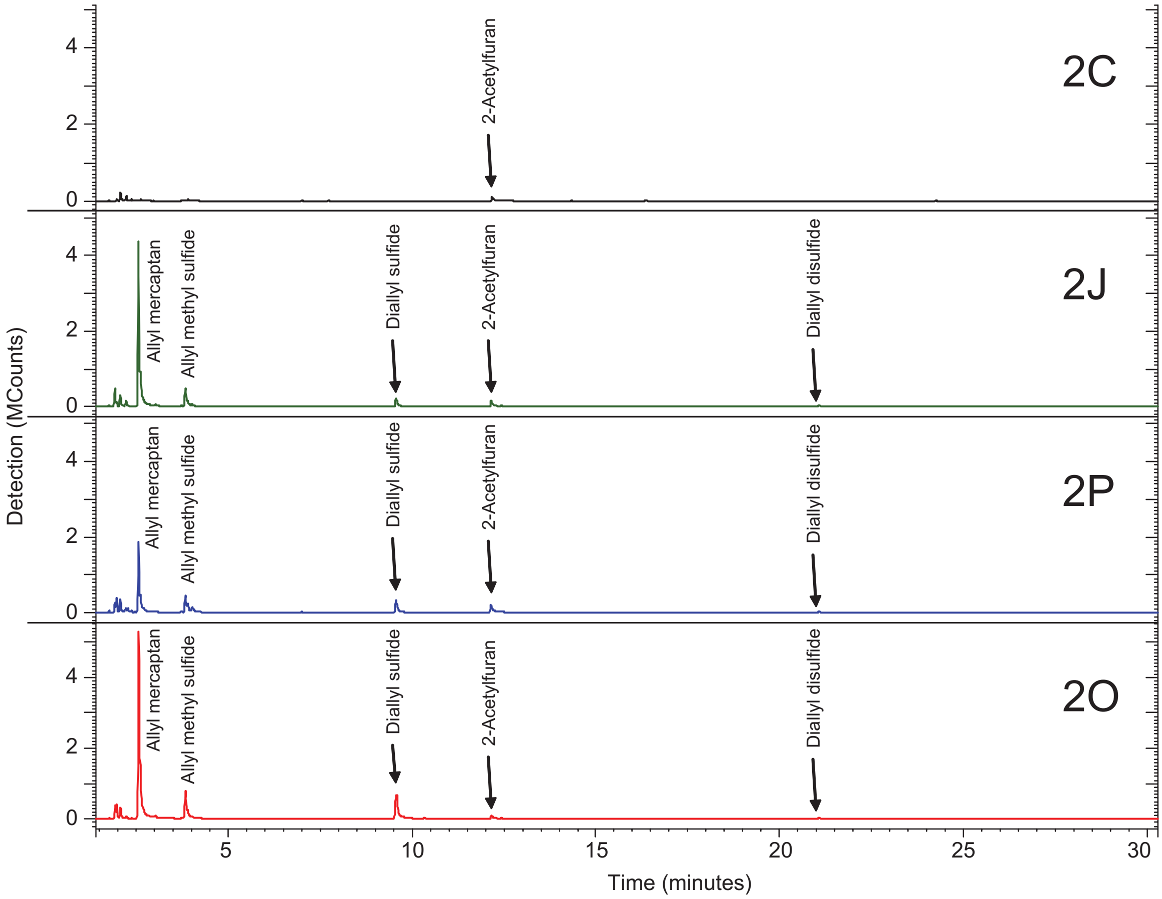
F-4. Sensory aroma profile of chicken-type flavor reactions with added garlic juice, garlic powder or garlic oil



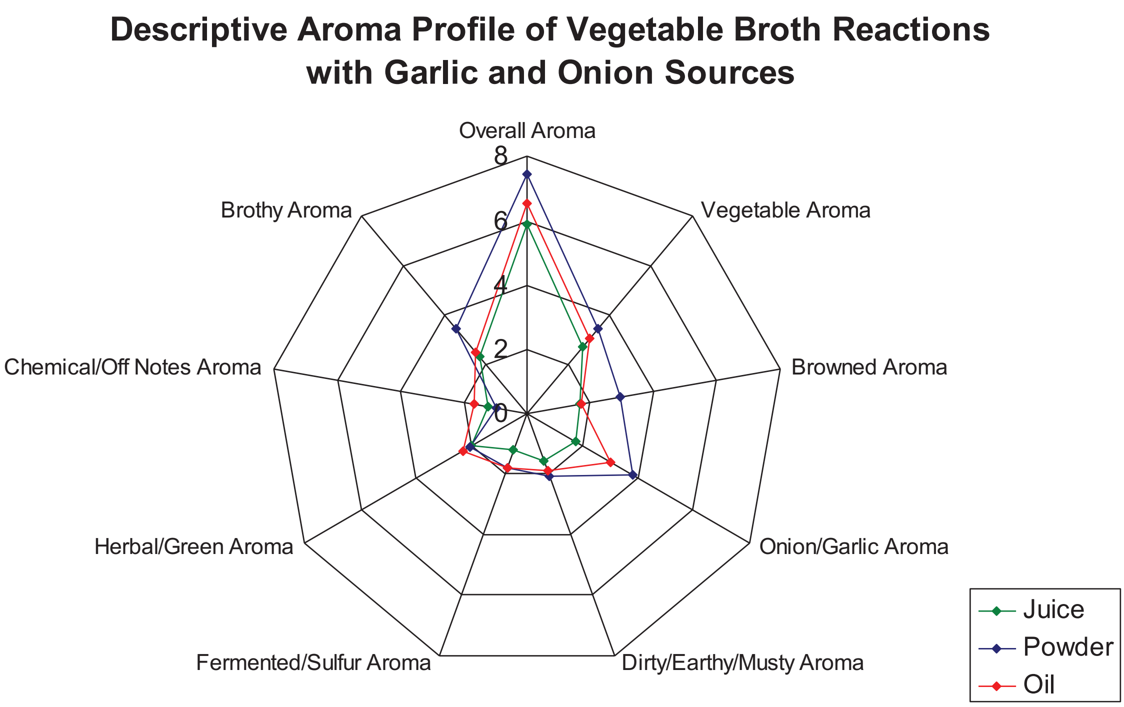
F-5. Sensory flavor profile of chicken-type flavor reactions with added garlic juice, garlic powder or garlic oil



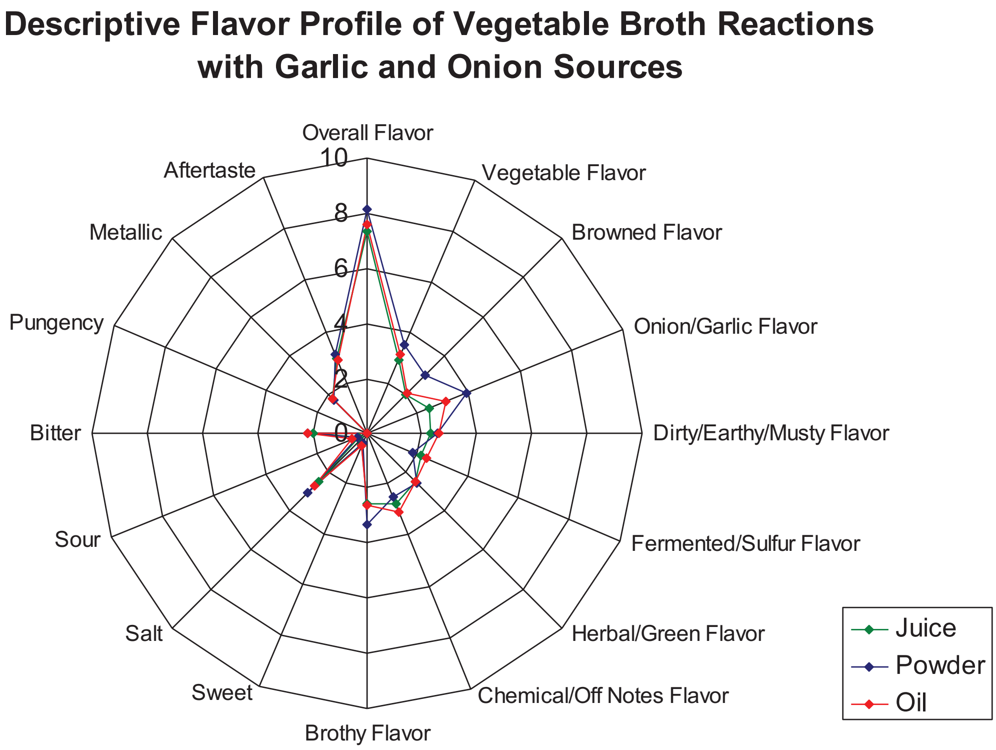
F-6. Headspace SPME GC/MS chromatograms of chicken-type flavor reactions with no garlic added (2C), or with added garlic juice (2J), garlic powder (2P), or garlic oil (2O)



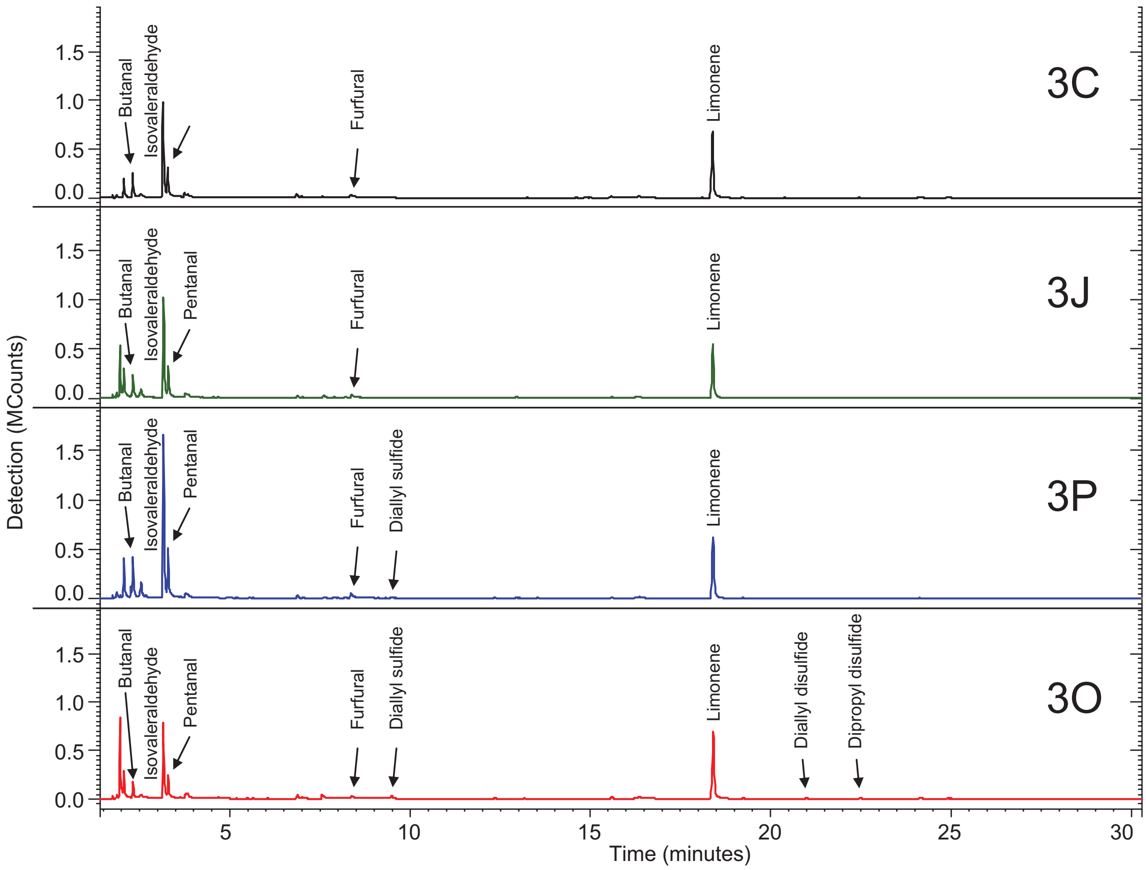
F-7. Sensory aroma profile of vegetable broth flavor reactions with added garlic/onion juice, garlic/onion powder or garlic/onion oil



F-8. Sensory flavor profile of vegetable broth flavor reactions with added garlic/onion juice, garlic/onion powder or garlic/onion oil



F-9. Headspace SPME GC/MS chromatograms of vegetable broth flavor reactions with no garlic/onion added (3C), or with added garlic/onion juices (3J), garlic/onion powders (3P), or garlic/onion oils (3O)



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broth flavors, possibly due to the additional Maillard reactants in the powders. They also had less fermented sulfur and chemical notes. The oils were second in onion and garlic flavor impact, but without the browning. The juices failed to have a great impact.

Analytically, we detected furfural, three aldehydes (butanal, isovaleraldehyde and pentanal) and limonene in all four vegetable broth reaction flavors. While sample 3J did not show much difference compared to sample 3C, samples 3P and 3O did have low levels of garlic and onion volatile sulfide compounds (**F-9**).

Conclusions

All of the allium extracts made noticeable contributions to the flavor of the reactions, but also had some notable limitations. Onion and garlic oils are by far the most concentrated means of imparting the flavor into the reaction, followed by powders, then juices. Using oils allows for more flexibility in formulating reactions, but also contributes other flavor notes that may limit their use. Powders are the best option if brown notes are desirable. The resulting residues need to be removed in oil-based reactions and need to be hydrated in aqueous reactions. The juices were dilute, but imparted the onion and garlic flavors to the glycerine-base reactions without the brown notes or the fermented/petroleum note. When using juices in the reaction, the flavor chemist needs much greater concentrations to be effective. Also, they are obligated to design the reaction with considerable amount of water, which affects the water activity of the reaction. Juices also need to be preserved, via freezing, or salt or acid addition. Flavor chemists may want to employ mixtures of oils, juices, and powders for customized flavor profiles.

The economics of using the different forms of allium extracts were not a focus of the study. After the study was completed, calculations using commodity pricing available to the authors demonstrated that the oils had the lowest cost in usage, followed by powders and juices. However, commodity prices can fluctuate widely, so flavor chemists need to factor in their own current costs.

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