



## Volatile and sensory profiling of cocktail bitters



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### ABSTRACT

Aromatic cocktail bitters are derived from the alcoholic extraction of a variety of plant materials and are used as additives in mixed drinks to enhance aroma and flavor. In this study sixteen commercial bitters were analyzed using volatile (GC–MS) and sensory profiling and multivariate statistics including Principal Component Analysis (PCA) and Partial Least Squares Regression (PLS). The samples differed significantly in their citrus, celery, and spice characteristics. 148 volatile compounds were tentatively identified and the composition varied significantly with the type of bitters sample evaluated. PLS analysis showed that the volatile data correlated well overall to the sensory data, explaining 60% of the overall variability in the dataset. Primary aldehydes and phenylpropanoids were most closely related to green and spice-related sensory descriptors. However, the sensory impact of terpenoid compounds was difficult to predict in many cases. This may be due to the wide range of aroma qualities associated with terpenes as well as to concentration, synergistic or masking effects.

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### 1. Introduction

Extracting plant matter into alcohol is an ancient process tracing to the Hippocratic wine of the Greeks (Tonutti & Liddle, 2010). As distilled liquor became more widely available, it was put to use in making plant extractions, mostly for medicinal purposes. Stoughton's Great Cordial Elixir, a distilled-alcohol based herbal extraction bittered with gentian root became available commercially in 1690. While this was a patent medicine marketed for its medicinal properties it is the closest ancestor of what we today know as bitters. The Elixir could be taken straight, although it was often diluted into wine to make “instant” *Purl-royal*, a popular drink resembling vermouth, and was also often subsequently mixed with straight or burnt brandy (brandy with sugar added and reduced in alcohol by igniting it). Adding Stoughton's Elixir to a dram of brandy yielded a “bitter draught” that was to be administered medicinally; recreational mixing soon followed (Wondrich, 2007). In present usage, bitters are generally used to add aroma complexity to an alcoholic cocktail drink, to complement and contrast the flavors already present in the component liquors, and, by selecting different styles, to subtly alter the flavor of the same base cocktail without changing its essence.

The commercial production of bitters dates to the early 1800s (Parsons, 2011), however production of many popular

nineteenth-century bitters ceased during Prohibition (Parsons, 2011). Following the repeal of Prohibition, several popular types were re-created from historical recipes using a variety of botanical ingredients (Table S1). Numerous types of bitters are now currently commercially available, although most contemporary manufacturers may only provide ingredients lists and actual formulas are not publicized.

Bitters are often informally categorized based on their aroma quality. ‘Aromatic’ styles, with spice flavors such as cinnamon, cloves, and cardamom are common. Anise flavored bitters are often noted as either a subtype of aromatic bitters or as a separate ‘New Orleans’ style named after their popular use in the so-called signature cocktail of New Orleans, the Sazerac (Bovis, 2012; Parsons, 2011; Sandham, 2012). A third important historic style is ‘Citrus’ bitters, especially orange-flavored bitters (Parsons, 2011). Finally, ‘Celery’ bitters with a predominant celery seed character are another style that had died out commercially until relatively recently (Baker, 1939).

Along with commercial reintroduction of defunct historical styles of bitters, since the early 2000s there has been an introduction of many new styles and types of bitters, driven in part by a rise in bartenders developing their own bitters in-house (Parsons, 2011; Sandham, 2012). While these “new bitters” have a range of ingredients and flavors with nearly indefinable boundaries, a number of recently invented styles have gained prominence. For example, bitters with the chocolate, chile, and cinnamon flavor profile of Mole Poblano, have been used widely at craft cocktail bars (Parsons, 2011). A similar “new classic” trend is more

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heavily-spiced bitters intended for Tiki drinks, which often use ingredients such as falernum (an almond and clove syrup) and pimento dram (an allspice liqueur) in conjunction with robust Jamaican or Agricole rums. It should be noted, however, there can be quite a bit of overlap in composition among the different styles; for example, many aromatic bitters recipes include citrus peel, and the included orange bitters recipe uses several spices. The ultimate flavor profile of any of these bitters products is therefore likely more dependent on proportions of ingredients than use of specific ingredients.

Gas chromatography combined with headspace solid phase microextraction (HS-SPME-GC-MS) is widely used for analysis of aroma volatiles of foods and beverages (Poole, 2012). Sensory descriptive analysis is a common tool for describing sensory attributes of commercial products (Lawless & Heymann, 2010). When combined with multivariate statistical analysis tools these approaches can be used to reveal important product-descriptor and sensory-chemical correlations (Lawless & Heymann, 2010).

The chemical and sensory profiles of bitters have not been previously reported. Therefore, the objectives of this study are to describe, map, and analyze the flavor chemistry of the most common styles of bitters currently available (16 commercial bitters representing at least two examples of each style (Aromatic, New Orleans-style, Citrus, Celery, Mole and Tiki; Table 1) using volatile profiling via Gas chromatography–mass spectrometry, sensory descriptive analysis with trained panelists, and multivariate statistical analysis.

## 2. Materials and methods

### 2.1. Samples

16 bitters (Table 1) were purchased from Astor Wines & Spirits (New York, NY), Cask (San Francisco, CA), Amor y Amargo (New York, NY), and Union Square Liquors (New York, NY).

### 2.2. Chemical analysis

200  $\mu$ L of bitters was pipetted into 10 mL of water in 20 mL amber glass headspace vials (Agilent Technologies, Santa Clara, CA) capped with magnetic, PTFE-lined silicone septa headspace caps. 2-Undecanone was used as an internal standard at 50  $\mu$ g/l (99% purity; Sigma–Aldrich). A conditioned, 2-cm long

PDMS-DVB-Carboxen SPME fiber (Supelco, Bellefonte, PA) was introduced into the headspace of the vial for 40 min at 25 °C with rotational shaking at 250 RPM. A Gerstel MPS2 autosampler (Mülheim an der Ruhr, Germany) performed the extraction and the injection. The fiber was removed from the headspace of the vial and immediately introduced into the inlet of an Agilent model 6890 GC-single quadrupole-MS (Agilent Technologies) with a DB-WAX column (30 m long, 0.25 mm ID, 0.25  $\mu$ m film thickness) (J&W Scientific, Folsom, CA). The inlet was held at 250 °C with a 10:1 split. The starting oven temperature was 40 °C, held for 3 min, followed by a 2 °C/min ramp until 180 °C was reached, then the ramp was increased to 30 °C/min until 250 °C was reached, and held for 3 min. The total run time was 47 min.

The mass spectrometer had a 1.5-min solvent delay and was run in scan mode with Electron Impact Ionization at 70 eV, from  $m/z$  40 to  $m/z$  300. The samples were analyzed in triplicate with relative standard deviations of replicate analysis of <10%. Peak identifications were made by matching the background-subtracted average mass spectrum across half peak height to the NIST 05 mass spectral database, followed by verification by retention index (calculated based on a series of C8–C20 hydrocarbons (Sigma–Aldrich, St. Louis, MO) analyzed at the same time) and pure standards where available. Following identification, GC peaks were manually integrated and converted into headspace concentration in  $\mu$ g/l 2-undecanone equivalents by dividing by the peak area by the 2-undecanone peak area.

### 2.3. Sensory analysis

A descriptive analysis procedure was used to profile the sensory characteristics of the bitters. A group of 14 panelists (10 Male, 4 Female, ages 21–35) were recruited from a pool of students and postdoctoral scholars in the department of Viticulture and Enology at the University of California, Davis. Over four training sessions, the panelists met in groups, smelled the bitters blind, and generated, discussed, and pooled descriptors by consensus until a final list of 30 terms was agreed upon. Samples were presented as 400  $\mu$ L bitters in 20 mL deionized water in opaque black wine-glasses. In the first training session, four of the bitters were smelled and discussed; in the second, third, and fourth sessions, six bitters were smelled and discussed, so that each bitters was smelled at least once during the training. Reference standards (Table 2) were made for each descriptor, and these were smelled and refined over

**Table 1**  
Samples used in the study, with historical sources and precedents, and style noted.

Name	Brand	Type	Code	
Boker's Bitters <sup>a</sup>	Dr. Adam Elmegirab	Aromatic	BOKERS	A1
Angostura Bitters <sup>b</sup>	Angostura	Aromatic	ANGOSTURA	A2
Jerry Thomas' Own Decanter Bitters <sup>c</sup>	Bitter Truth	Aromatic	JTDECANTER	A3
Whiskey Barrel-Aged Bitters	Fee Brothers	Aromatic	WHISKEY BARREL-AGED	A4
Regan's Orange Bitters Number 6 <sup>d</sup>	Buffalo Trace	Citrus	REGAN'S ORANGE	C1
Hopped Grapefruit Bitters	Bittermen's	Citrus	HOP-GRAPEFRUIT	C2
Grapefruit Bitters	Scrappy's	Citrus	SCRAPPY GRAPEFRUIT	C3
Orange Bitters	Scrappy's	Citrus	SCRAPPY ORANGE	C4
Xocolatl Mole Bitters	Bittermen's	Mole	XOCOTL MOLE	M1
Mole Bitters	Bitter Truth	Mole	BT-MOLE	M2
'Elamakule Tiki Bitters	Bittermen's	Tiki	ELAMAKULE-TIKI	T1
Jamaica Bitters	Bittercube	Tiki	JAMAICA	T2
Creole Bitters	Bitter Truth	New Orleans	BT-CREOLE	NO1
Peychaud's Bitters <sup>b</sup>	Peychaud	New Orleans	PEYCHAUD	NO2
Orchard St Celery	Bittermen's	Celery	BMCELERY	C1
Celery Bitters	Scrappy's	Celery	SCRAPPYCELERY	C2

<sup>a</sup> Based on historical recipe for now-defunct Boker's brand.

<sup>b</sup> 9th century brand.

<sup>c</sup> Based on historical recipe from Jerry Thomas, *The Bon Vivants Companion or How to Mix Drinks*.

<sup>d</sup> Based on historical recipe from Charles H. Baker, *The Gentleman's Companion: Being an Exotic Drinking Book or Around the World with Jigger, Beaker and Flask*.

**Table 2**  
Sensory terms and references used in the descriptive analysis.

Descriptor	Reference
Aroma intensity	Overall intensity (no physical reference)
Cardamom	4 crushed green cardamom pods
Grapefruit	2 cm * 8 cm strip fresh grapefruit peel, oils manually expressed into glass first
Molasses	10 mL molasses
Chocolate	10 g shaved dark chocolate (Valhrona)
Celery seed	2 g celery seeds, crushed
Cola	20 mL cola (Coca-Cola)
Soapy	1 g unscented ivory soap
Root beer	20 mL root beer (Virgil's)
Orange candy	5 orange jelly beans, halved (Jelly Belly)
Green	2 g each fresh cilantro leaf, fennel, and cucumber, bruised
Tea	2 g black English Breakfast tea leaves (Peet's)
Brown sugar	5 g brown sugar (C&H)
Lime peel	1 cm * 5 cm strip fresh lime peel, oils expressed manually into glass first
Black pepper	6 black peppercorns, lightly crushed
Alfalfa hay	1 g dry alfalfa
Juniper	3 dried juniper berries, crushed
Mint	2 fresh peppermint and 2 spearmint leaves
Ginger	2 cm * 2 cm * 3 cm piece of fresh ginger, minced
Orange peel	2 cm * 8 cm strip fresh orange peel, oils manually expressed into glass first
Earthy	5 g freshly dug soil with 2 mL water
Dried fruit	10 golden raisins, 2 dried apricots, 2 dried cherries
Anise	1 star anise pod
Cinnamon	2 g cinnamon powder
Wood	2 g medium toasted oak chips (Evoak)
Clove	3 cloves
Nutmeg	1 g shaved nutmeg pod
Caraway	1 g caraway seeds, lightly crushed
Vanilla	2 cm length vanilla pod + 500 µL vanilla extract (Nieman-Massey)
Chile	1 g dried ancho chile, chopped

the second, third, and fourth sessions. Over two additional sessions, the descriptors and references were fixed and the panelists analyzed the intensity of each descriptor for each bitters in a training exercise in sensory booths. The descriptive analysis proper was performed in triplicate, with each panelist smelling each reference, then rating the intensity of the aroma of each reference in each bitters over six sessions on an unstructured 9-cm line scale from “low intensity” to “high intensity.” The panelists were presented with eight samples per session, in lidded opaque black wineglasses under red light with random 3-digit codes as labels in a Williams Latin Square presentation design. Descriptive analysis was performed using FIZZ (Biosystèmes, Couternon, France).

#### 2.4. Statistical analysis

The sensory data was subjected to a 3-way analysis of variance (ANOVA) with 2-way interactions for all 30 descriptors in the R statistical package. The main effects were product, judge, and replicate. For descriptors with a significant Judge \* Product interaction, a pseudo-mixed model (with Mean Square of Judge \* Product replacing Mean Square of Error in the *F*-value calculation for Product effect) was used. Products were considered significantly different in a given aroma when  $p < 0.05$ . For significant descriptors, mean values for each descriptor-product pair were calculated over all judges and replicates and a Principal Component Analysis (PCA) was performed on the mean data in R. Mean values for descriptors and mean peak areas from GC normalized to internal standard areas were analyzed with Partial Least Squares Regression (PLS) in Unscrambler, with the sensory data being set as the dependent variable to the independent-variable GC dataset. For purposes of data interpretation, aroma descriptors referenced

for individual compounds were taken from the Perflavory website (W. Luebke, Perflavory; <http://www.perflavory.com>; accessed 20 August, 2014).

### 3. Results and discussion

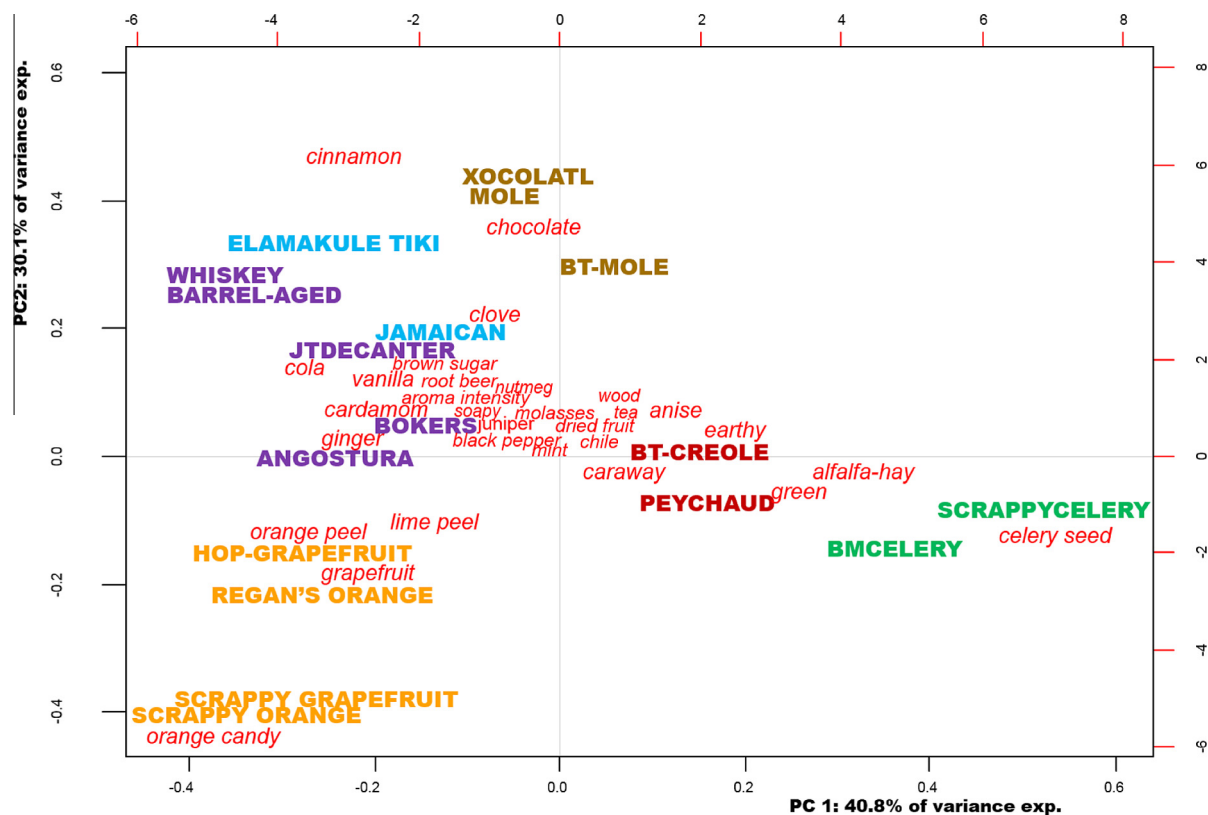
#### 3.1. Sensory analysis

The panel agreed upon 30 aroma descriptors for the bitters, listed in Table 2 with the corresponding references. Of these, all except *nutmeg* were significantly different, ANOVA ( $p < 0.05$ ). Many of the descriptors, such as *clove*, *cinnamon*, and *celery seed* reflected ingredients commonly used in bitters. Others, such as *cola*, *soapy*, *root beer*, and *earthy*, reflected non-ingredient aromas that may arise from perceptual blending of the mixtures. Mean sensory intensity for each attribute is provided in Table S2.

Principal Component Analysis (Fig. 1) was performed to describe latent interrelationships among the bitters samples and aroma descriptors. Together the first two dimensions account for 71% of the sensory variance among the bitters samples. In the PCA the bitters samples are separated into roughly 3 “lobes” or groups; PC 1 (the *x*-axis) accounts for 40.8% of the variance and represents a continuum from orange/citrus aromas on the left to green/celery aromas on the right with spice-related and other aromas in the middle. PC 2 (the *y*-axis) accounts for 30.2% of the variance and represents a continuum from botanical notes from citrus and plants on the bottom to *chocolate*, *cinnamon*, and other spice aromas at the top. The bitters were separated fairly well by category; the Citrus bitters (orange-colored text) grouped together as did (separately) the Celery (green-colored text) and New Orleans-style bitters (maroon-colored text). The Aromatic (purple text), Tiki, (light blue text) and Mole-style (brown text) bitters grouped close to each other, with some overlap, with, for example, the cinnamon-heavy Mole bitters grouping close to the similarly *cinnamon*-forward ‘Elamakule Tiki’ and ‘Whiskey-Barrel Aged’ Bitters. Angostura and especially Boker’s (purple text) bitters both plotted very close to the center of the plot, suggesting that as a style they are close to a kind of “average” style or are blended such that no one aroma descriptor dominates their flavor.

#### 3.2. Gas chromatography–mass spectrometry

148 compounds were identified or tentatively identified across the set of bitters, with a minimum of 19 compounds, a maximum of 78 compounds, and a mean of 46 compounds per sample of bitters. The compounds identified included aldehydes; simple aromatic compounds; esters; terpenes and sesquiterpenes, and derivatives thereof (alcohols, acetates, esters, etc.); and phenylpropenes. A list of compounds can be found in Table 3, with their relative headspace concentrations (in 2-undecanone µg/l equivalents) in Table S3. Twenty-three of these compounds were detected in only one sample out of the sixteen, while in aggregate each compound was detected in an average of five of the samples (SD = 3.96). The most common compounds were:  $\alpha$ -pinene, camphene,  $\beta$ -pinene,  $\beta$ -myrcene, beta-phellandrene, octyl acetate, ethyl nonanoate, ethyl benzoate, geranyl acetate, and safrole (B123), present in nine samples; alpha-thujene (B15), neryl acetate, nerolidol, eugenol, and an unidentified compound (“ni.j”), present in ten samples; caryophyllene, myristicin, and an unidentified compound (“ni.d”), present in eleven samples; octanal, ethyl octanoate, anethole and methyleugenol, present in twelve samples; gamma-terpinene, alpha-terpinyl acetate, *p*-cymene, and terpinolene present in thirteen samples; limonene, eucalyptol, linalool, and bornyl acetate, present in fifteen samples; and decanal, present in all sixteen samples. A number of these highly shared



**Fig. 1.** Principal Component Analysis (PCA) of bitters. PC 1 (x-axis) explains 40.8% of variance in sensory data; PC 2 (y-axis) explains 30.2% of variance. Sensory descriptors are in red italicized text. Samples are in bold capital letters, coded by style: Citrus in orange, Aromatic in purple, Tiki in blue, Mole in brown, New Orleans-style in dark red, and Celery in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compounds vary in relative levels across the dataset by several orders of magnitude. For example, decanal was detected in all samples, but there is a 448-fold difference in relative headspace levels between the samples with the least (Peychaud's) and most (Scrappy's Orange) decanal. Limonene, detected in fifteen out of the sixteen samples, shows a similarly high 598-fold difference in relative headspace levels, between 'Elamakule Tiki (least) and Scrappy's Celery (most). Anethole has a 634-fold difference in relative headspace amount between Bitter Truth's Creole bitters and Bittermen's Celery.

As is the case for many other alcoholic beverages incorporating multiple plant products (for example, gin, absinthe, or chartreuse), the exact formulations of commercially sold bitters are generally kept entirely or partially secret by the companies that make them (Tonutti & Liddle, 2010). This means that the volatile profiles characterized in the current work cannot be compared directly to volatile profiles of the plant products used in each sample, because the complete lists of plant products and their proportions used are not made publicly available.

However, while exact formulations are not available, several historical recipes that have inspired current formulations are available. Botanicals commonly used in bitters, with use in specific recipes or other sources are provided (Table S1). Boker's Bitters, Jerry Thomas' Own Decanter Bitters, and Orange Bitters are all historical versions of samples used in this study (A1, A3, and C1, respectively) and Stoughton's Bitters is a 19th-century version of Stoughton's Great Cordial Elixir, the patent medicine first marketed in 1690 that was a precursor to cocktail bitters (Wondrich, 2007). Table 4 contains reported volatile compositions of a subset of fourteen of these ingredients, each used explicitly in at least one bitters recipe, with the ten most abundant volatiles (where available) listed with their relative abundances. Often, herbal components

are designated separately as "bitting" and "flavoring" agents (Parsons, 2011), with "bitting" components being less frequently analyzed for their volatiles. However, in the case of gentian and cinchona, common as bitting agents, volatile profiling has been performed (Chialva, Frattini, & Martelli, 1985, 1986) which shows that these "bitting" agents also produce a number of compounds which may contribute to the aroma of bitters which use them in their recipe. A number of the compounds detected in a majority of the samples—decanal, limonene, nerol, eugenol, eucalyptol, linalool, gamma-terpinene, caryophyllene, cymene, and anethole—are major components of one or several of these named and commonly used plant ingredients.

In some cases, a compound was present in a few samples at relatively similar amounts—for example, alpha-curcumen was detected in four samples, within a 1.5-fold range of levels, which could mean that the material(s) used in the recipes for these samples that contained alpha-curcumen were simply not used for the other samples in which the compound was not detected. Conversely, the presence of limonene in almost every sample, but in a range covering nearly three orders of magnitude, could reflect several different paths to the presence of limonene in bitters, which are generalizable for other compounds present in multiple ingredients. Limonene is a component of many ingredients commonly used for bitters, for example sweet orange, cardamom, gentian, caraway, cinchona, coriander, lemon, and bitter orange, and so its total amount in for example, orange bitters, will come from the additive contributions of the limonene extracted from multiple sources, in this case, orange peel, cardamom, gentian, caraway, cinchona, and coriander. A high level of limonene in one sample could be from, for example, the use of one material (e.g., citrus peel) that is very high in limonene, or from the use of several materials each with an intermediate concentration of limonene. Contributions of

**Table 3**  
Compounds identified by GC–MS in samples of bitters.

#	Name <sup>a</sup>	CAS	RT	CRI	Literature RI		
					Pherobase	Flavornet	Other
B1	2-Methylbutanal	s	96-17-3	3.12	831	864	912
B2	3-Methylbutanal	s	590-86-3	3.18	903	912	910
B3	Ethyl propanoate	s	105-37-3	3.85	920	950	951
B4	Ethylisobutyrate	s	97-62-1	4.03	940	955-972	955
B5	Alpha-thujene		2867-05-2	5.52	1014	1038	1021
B6	Alpha-pinene	s	80-56-8	5.54	1014	1027-1034	1032
B7	2-Butanol	s	78-92-2	5.65	1018	1022	
B8	Toluene	s	108-88-3	5.76	1021	1042	
B9	Ethyl butanoate	s	105-54-4	5.86	1024	1022-1057	1028
B10	Ethyl 2-methylbutyrate	s	7452-79-1	6.41	1040	1056-1069	1050
B11	Camphene	s	79-92-5	6.63	1047	1077	1075
B12	Ethyl isovalerate	s	108-64-5	7.15	1063	1053-1082	1060
B13	Hexanal	s	66-25-1	7.30	1067	1067-1093	1084
B14	Isobutanol	s	78-83-1	8.00	1088		1099
B15	Alpha-thujene		2867-05-2	8.32	1097	1038	1059
B16	ni.a			8.44	1101		
B17	Sabinene		3387-41-5	8.69	1106	1123	
B18	Isoamyl acetate	s	123-92-2	9.00	1112	1118-1147	1117
B19	Ethyl pentanoate	s	539-82-2	9.53	1123	1120-1170	1133
B20	3-Carene	s	13466-78-9	9.87	1130	1148	1148
B21	Beta-pinene	s	127-91-3	10.59	1144	1113-1124	1116
B22	Beta-myrcene	s	123-35-3	10.72	1147	1161-1187	1145
B23	Sabinene		3387-41-5	10.72	1147	1178	1178
B24	Heptanal	s	111-71-7	11.85	1170	1197	1174
B25	Limonene	s	138-86-3	12.40	1181	1198-1234	1201
B26	Beta-phellandrene	s	555-10-2	12.53	1184	1241	1209
B27	Eucalyptol	s	470-82-6	12.57	1184	1214-1224	
B28	Isoamyl alcohol	s	123-51-3	12.88	1191	1169-1247	1205
B29	Ethyl hexanoate	s	123-66-0	13.89	1220	1224-1270	1220
B30	Beta-trans-ocimene		3779-61-1	13.90	1221	1242	1242
B31	Gamma-terpinene		99-85-4	14.16	1226	1262-1265	1238
B32	ni.b			14.32	1230	1555	
B33	Styrene (cinnamene)		100-42-5	14.41	1232	1273	1241
B34	cis-beta-ocimene		3338-55-4	14.59	1236	1225-1245	1245
B35	p-Cymene		527-84-4	15.14	1248	1267	1261
B36	Hexyl acetate	s	142-92-7	15.61	1259	1264	1270
B37	Terpinolene		586-62-9	15.78	1262	1275-1297	1284
B38	Octanal	s	124-13-0	16.20	1272	1300-1307	1280
B39	1-Octen-3-ol	s	3391-86-4	16.59	1280	1305-1323	1285
B40	ni.c			16.72	1283		
B41	E-2-Heptenal		18829-55-5	17.67	1301	1336	
B42	Ethyl-E-3-hexenoate		26553-46-8	17.88	1309	1301	
B43	ni.d			17.98	1312		
B44	Ethyl heptanoate	s	106-30-9	18.10	1315		
B45	6-Methyl-5-heptene-2-one	s	110-93-0	18.29	1319	1319	
B46	ni.e			19.36	1343		
B47	ni.f			20.06	1359		
B48	Heptyl acetate	s	112-06-1	20.13	1360	1370	
B49	ni.g			20.28	1364		
B50	Fenchone		1195-79-5	20.60	1371	1402-1410	
B51	ni.h			20.64	1372	1560	
B52	Nonanal	s	124-19-6	20.83	1376	1402-1415	1385
B53	ni.i			21.07	1392		
B54	Benzene, pentyl-		538-68-1	21.84	1400	1433	
B55	Alpha,p-dimethylstyrene		1195-32-0	22.39	1412		1414
B56	Ethyl octanoate	s	106-32-1	22.81	1422	1422-1446	1436
B57	ni.j			23.11	1429		
B58	Linalool oxide	s	5989-33-3	23.24	1432	1423	
B59	p-Methone		89-80-5	23.50	1438	1440	
B60	Fenchyl acetate		13851-11-1	23.86	1447	1443	
B61	Methyl nonanoate	s	1731-84-6	23.88	1448	1487	
B62	trans-Sabinene-hydrate		17699-16-0	24.09	1453	1459	
B63	ni.k			24.25	1456		
B64	Octyl acetate	s	112-14-1	24.48	1462	1478	
B65	Menthone	s	14073-97-3	24.62	1465	1454-1478	
B66	Copaene		3856-25-5	24.85	1471	1488	
B67	ni.l			24.90	1472		
B68	Alpha-cubebene		17699-14-8	25.15	1478	1463-1480	
B69	Decanal	s	112-31-2	25.32	1482	1447-1510	
B70	Camphor	s	76-22-2	25.40	1484	1498	
B71	Methyl nonanoate	s	1731-84-6	25.42	1484	1487	
B72	Benzaldehyde	s	100-52-7	25.59	1488	1525	1495
B73	ni.m			26.00	1498	1753	
B74	ni.n			26.60	1513		
B75	Ethyl nonanoate	s	123-29-5	27.00	1523	1528	

(continued on next page)

Table 3 (continued)

#	Name <sup>a</sup>	CAS	RT	CRI	Literature RI		
					Pherobase	Flavornet	Other
B76	Linalool	s 78-70-6	27.50	1535	1484–1570		
B77	Methyl decanoate	s 110-42-9	27.68	1540	1590		
B78	Isomenthyl acetate	20777-45-1	27.82	1543			1597 <sup>b</sup>
B79	Linalyl acetate	s 115-95-7	27.96	1547	1569		
B80	1-Octanol	72-69-5	27.97	1547	1557–1566	1553	
B81	Bornyl acetate	76-49-3	28.34	1556	1580		
B82	Nonyl acetate	143-13-5	28.62	1563	1585		
B83	Caryophyllene	s 13877-93-5	28.90	1570	1608–1618		
B84	Alpha-bergamotene	13474-59-4	28.97	1572			1570, 1586 <sup>c</sup>
B85	Undecanal	s 112-44-7	29.51	1585	1624		
B86	Lavandulyl acetate	20777-39-3	30.02	1598	1597		
B87	Acetophenone	s 98-86-2	30.41	1608		1645	
B88	Methyl 4-decenoate	7367-83-1	30.63	1614	1622		
B89	Decanal diethyl acetal	34764-02-8	30.79	1618			
B90	Menthol	s 89-78-1	30.98	1623	1626		
B91	Ethyl decanoate	s 110-38-3	31.04	1625	1630	1655	
B92	(-)-trans-Pinocarvyl acetate	33045-02-2	31.24	1630	1638		
B93	ni.o		31.39	1634			
B94	Ethyl benzoate	s 93-89-0	31.42	1635		1648	
B95	Estragole	140-67-0	31.61	1640		1655	
B96	Humulene	6753-98-6	31.62	1640	1680		1663
B97	Citronellyl acetate	150-84-5	31.78	1645	1607–1663	1607	
B98	E-beta-farnesene	s 18794-84-8	31.95	1649	1658–1674		
B99	Alpha-himchalene	3853-83-6	32.28	1658	1649		
B100	isolongifolan-8-ol	1139-08-8	32.36	1660			
B101	alpha-terpinyl acetate	80-26-2	32.80	1672	1700		
B102	Gamma-murolene	30021-74-0	32.80	1672	1684		
B103	Beta-eudesmene	17066-67-0	32.83	1672	1711		
B104	Decyl acetate	112-17-4	32.90	1674	1691		
B105	p-Menth-1-en-8-ol	s 98-55-5	32.95	1682	1669–1720	1688	
B106	Gamma-selinene	515-17-3	32.98	1686	1724	1711	
B107	Eremophilene	10219-75-7	33.50	1690			1744 <sup>d</sup>
B108	Dodecanal	s 112-54-9	33.53	1691	1700–1722		
B109	Alpha-murolene	31983-22-9	33.83	1699	1727	1714	
B110	Carvone	s 99-49-0	33.96	1703	1715	1720	
B111	Alpha-selinene	473-13-2	34.01	1704	1724		
B112	Nerol acetate	141-12-8	34.09	1706	1728		
B113	ni.p		34.81	1726	1808		
B114	Beta-cadinene	523-47-7	35.00	1731	1749–1752		
B115	Geranyl acetate	s 105-87-3	35.22	1737	1711–1760		
B116	ni.q		35.68	1750			
B117	Perilla aldehyde	2111-75-3	35.70	1750	1797	1765	
B118	Citronellol	s 106-22-9	35.79	1753	1737–1786		
B119	Alpha-curcumene	644-30-4	35.84	1771	1777	1773	
B120	Nerol	s 106-25-2	37.99	1780	1753–1770	1770	
B121	Anethole	s 104-46-1	37.25	1793	1808		
B122	Calamene	1406-50-4	37.55	1801	1826–1837		
B123	Safrole	s 94-59-7	38.75	1836			1863 <sup>b</sup>
B124	Alpha-calacorene	21391-99-1	40.62	1889	1906–1916		
B125	Caryophyllene oxide	s 1139-30-6	42.52	1969	1999		
B126	Perilla alcohol	536-59-4	42.73	1979			2003 <sup>b</sup>
B127	Methyleugenol	s 93-15-2	42.94	1988			2007 <sup>b</sup>
B128	Safrole	s 94-59-7	43.05	1994			
B129	Cinnamaldehyde	104-55-2	43.11	1996	2017		
B130	Nerolidol	7212-44-4	43.44	1998	1961–2054		
B131	cubenol	21284-22-0	43.58	>2000		1993	
B132	Ethyl tetradecanoate	s 124-06-1	43.62	>2000		2042	
B133	Elemol	8024-27-9	43.83	>2000	2089		
B134	Cinnamyl acetate	103-54-8	44.25	>2000	2104		
B135	Eugenol	s 97-53-0	44.37	>2000	2141–2192	2141	
B136	Eudesmol	473-15-4	44.47	>2000	2182		
B137	Tau-cadinol	5937-11-1	44.53	>2000	2165		
B138	Tau-murolol	19912-62-0	44.57	>2000	2178		
B139	Carvacrol	499-75-2	44.67	>2000			2206 <sup>b</sup>
B140	Elemicin	487-11-6	44.85	>2000			2167 <sup>b</sup>
B141	Beta-eudesmol	473-15-4	44.92	>2000	2248		
B142	Eugenol acetate	93-28-7	44.93	>2000			
B143	Myristicin	607-91-0	45.06	>2000			2257 <sup>b</sup>
B144	Isoeugenol	s 97-54-1	45.47	>2000	2365–2367		
B145	ni.r		46.11	>2000			
B146	Apiol	523-80-8	46.69	>2000			
B147	Nootkatone	s 4674-50-4	46.84	>2000	2573		
B148	Benzyl benzoate	120-51-4	47.42	>2000		2071	

s = matched to authentic standard.

CRI = Calculated Retention Index

<sup>a</sup> Mass spec matched by NIST > 80%.<sup>b</sup> Lee, Umano, Shibamoto, and Lee (2005).<sup>c</sup> Jones et al. (2011).<sup>d</sup> Nakata et al. (2013).

one compound from several botanical sources may lead to concentration- and mixing-dependent sensory attributes that are not present in any of the raw materials. Chemical-sensory relationships are discussed further, below.

### 3.3. Linking chemical and sensory profiles

Samples made with multiple aromatic plant components, such as bitters, have complex chemical compositions with many overlapping compounds among samples as well as many “orphan” compounds present in only one or a few samples. They also have complex aromas, with multiple, differing sensory characteristics and many compounds contributing to these sensory characteristics. While some of these sensory characteristics may have strong correlations to one particular compound (and vice versa), it is likely that perceptual interactions involving multiple compounds and multiple aromas play a role in the overall flavor of these samples. Given that many independent variables (volatile molecules) are interacting to produce many dependent variables (aromas), multivariate regression is an ideal tool to visualize and begin to understand these complex, interacting relationships. To model how differences in sensory characteristics are produced by variations in volatile composition, a Partial Least Squares regression (PLS) was performed on the sensory and volatile datasets on bitters (Fig. 2). The PLS identifies variance in the volatile (independent-variable) dataset, and uses it to explain as much as possible of the variance it identifies in the sensory (dependent-variable) dataset. In this way, two types of variance are explained: the independent-variable variance, and the dependent-variable variance.

In this particular regression analysis, the first two principal components explained 23% of the independent, chemical variables (13% in PC1 and 10% in PC2), but this 23% of variance was able to explain 60% of the variance in the sensory dataset (36% in PC1, 24% in PC2) (Fig. 2). This means that the relationship between chemistry and aroma in these samples of bitters is complex enough that, when chemical data is taken into account, two Principal Components capture about 10% less of the variance in the sensory dataset than in the sensory-only PCA, which explained 70% of the variance in the first two PCs. Conversely, this also means that a relatively small amount of the variance in chemistry (23%) is able to explain a large portion of the sensory variance, and explain it spatially in such a way that mimics the spatial explanation provided by the sensory-only.

The general shape of the sensory PCA is preserved in the PLS (Fig. 2A); with the first latent variable (PC1), the *x*-axis, defined by the contrast from citrus on the left to celery on the right, with herbal and spicy aromas in the middle; and with the second latent variable (PC2), the *y*-axis defined by the progression from more citrus- and green-type aromas on the bottom of the biplot and spicy and *chocolate* aromas on the top of the biplot. In terms of the placement of the bitters samples themselves, the 3-lobed grouping is somewhat preserved, with (working counterclockwise from approximately the lower left quadrant) Citrus, Celery-New Orleans, and Aromatic-Tiki-Mole in the same fairly distinct areas as in the PCA. However, there is more overlap between these groups in the PLS – the Regan’s Orange and Angostura positions create overlap between the Citrus group and the Aromatic group, and there is more overall intercalation between the Tiki, Aromatic, and Mole groups. The distribution of volatiles in the plot (Fig. 2B and C) mimics the 3-lobed shape of the samples and the sensory descriptors, with some compounds plotting between groupings of samples. Limonene, for example, is present at a high relative amounts in both Citrus and Celery bitters (Table S3), and is located between these two groups of samples in the plot.

The sample set contains volatiles from several classes of compounds, with aliphatic aldehydes, phenylpropenes, terpenoids,

and sesquiterpenoids being the four most abundant of these. Generally, there is not a strong association between any chemical class overall and a particular sensory characteristic, sample, or area of the plot. This means that, within this dataset, there aren’t “terpenic” or “aldehydic” flavors so much as trends, associations, and differences within each chemical classes correlating to sensory differences in samples.

In some cases the spatial relationships between sensory descriptors and compounds are directly relatable to aroma characteristics of the compounds in isolation. For example, the (aliphatic, non-terpenic) aldehydes separate into roughly three groups, mimicking the partitioning of the dataset as a whole into three groups. Along the citrus-related “arm,” with the descriptors *lime peel*, *orange peel*, *grapefruit*, and *orange candy*, dodecanal, octanal, decanal, and nonanal, are grouped together. All of these compounds, when isolated have some citrusy (as well as fatty) aroma characteristics (T. Acree & H. Arn, Flavornet, <http://www.flavornet.org>; accessed 20 August, 2014). Conversely hexanal and heptanal group with the *green*, *alfalfa-hay*, and *celery seed* descriptors, suggesting that their “greener” (T. Acree & H. Arn, Flavornet, <http://www.flavornet.org>; accessed 20 August, 2014; W. Luebke, Perflavory; <http://www.perflavory.com>; accessed 20 August, 2014) aroma characteristics are more emphasized in these samples. Octanal and nonanal are also described as having partially green aromas, but their citrus characteristics are emphasized in these samples. C6–C12 aldehydes appear to generally decrease in green qualities and increase in citrus qualities in these bitters as chain length increases. 2- and 3-Methylbutanal, which are described as having some chocolaty and nutty characteristics (Flavornet, Perflavory) group with the aroma descriptors that include *chocolate*.

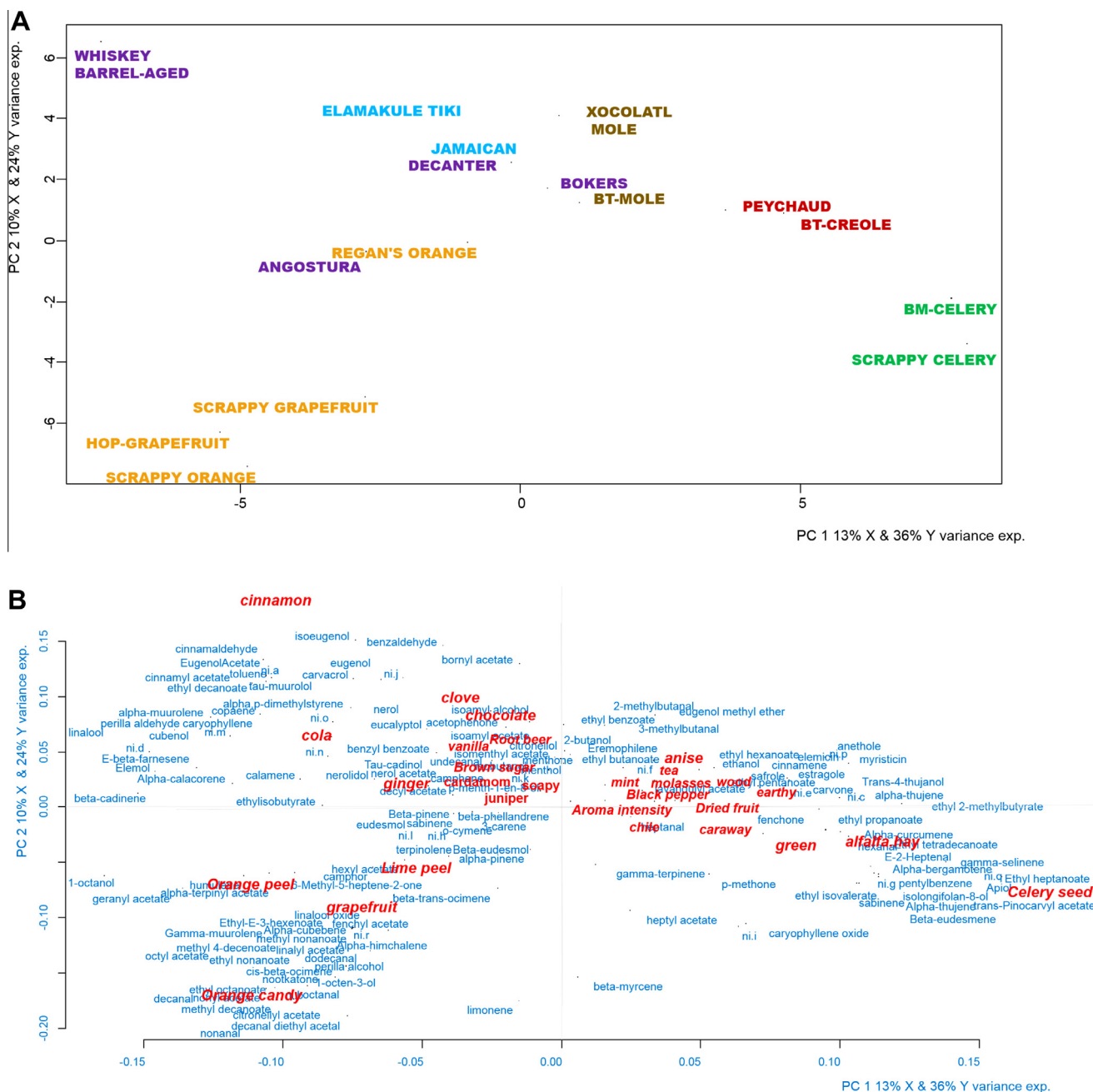
A similarly well-defined trend can be seen for the phenylpropenes, a class of aromatic compounds with a conserved allylbenzene structure and various other functional groups. Unlike the aldehydes, which separate into three groups, the phenylpropenes map more like a continuum along, roughly, low PC1-high PC2 to high PC1-low PC2. The low-PC1/high PC2 phenylpropenes are eugenol derivatives, have similar clove-spicy type aromas, and overlap with the Aromatic-Tiki-Mole group of bitters, and the *spice-cola-chocolate* group of aroma descriptors. Further along PC1, anethole, estragole, chavicol, safrole, isosafrole, and myristicin group with the New Orleans bitters and the far right edge of the Aromatic/Mole bitters, as well as the *anise*, *nutmeg*, *woody*, *caraway*, *green*, and *alfalfa-hay* aroma descriptors. While these compounds are not as chemically similar overall as the eugenol group, they on their own tend to have woody-anise like characteristics with some spiciness, which lines up conceptually with their proximate aroma descriptors in the PLS. Finally, apiol, which has an herbal-parsley aroma (Perflavory) and is found in dill, parsley, and celery, plots on its own with an extremely strong correlation to the *celery seed* descriptor.

With the esters, terpenes, and sesquiterpenes, the relationships between compounds and aromas are more complicated to explain than for aldehydes and phenylpropenes. This may arise from a number of factors – for one, the esters, terpenes, and sesquiterpenes encompass more compounds per group than the other compound classes, and so each class encompasses more points on the plot. This means that while the shape of the chemical data – terpenes, sesquiterpenes, and esters alike – mimics the shape of the sensory product/attribute data, there are enough compounds plotted and enough diversity in their aroma, even between fairly proximal compounds, that trends are not immediately visible.

Another factor contributing to the complexity of the terpene, sesquiterpene, and ester PLS data may have root in the odor complexity and conceptual similarity of the compounds within these groups. While the relationship between odorant structure and odor quality is complex and poorly understood, recent research has







**Fig. 2.** Plots of Partial Least Squares Regression (PLS) analysis of bitter volatile composition and sensory qualities by descriptive analysis. (A) Positions of samples. (B) Biplot of sensory descriptors (red) and volatiles (blue). (C) Exploded view of compounds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

shown that molecular complexity of odorants tends to correlate with odor complexity – specifically, odorants with greater molecular complexity tend, by both experts and naïve panelists, to require more terms for their full description compared to odorants with lesser molecular complexity (Kermen et al., 2011).

Some of the correlations between terpene compounds and aroma descriptors appear straightforward – the association of the strongly orange-smelling limonene and grapefruit-smelling nootkatone with the citrus descriptors, for example. Non-substituted terpenes tend to plot towards the negative side of PC2, though there are a few on the positive end of PC2, while oxygenated terpenes (alcohols, aldehydes, ketones, and oxides) appear scattered over the whole area of the PLS plot, with a small area in the

*cinnamon-cola* dominated low PC1-high PC2 quadrant containing mostly these oxygenated terpenes and not other terpenes. Finally, the terpene acetates appear in all three primary lobes of the PLS – citronellyl-, geranyl- and alpha-terpinyl acetate with the citrus group, bornyl acetate with the spicy group, and pinocarvyl acetate with the celery-green group. A similar trend, or rather, lack thereof, is evident with the sesquiterpene compounds, with both unsubstituted and oxygenated sesquiterpenes appearing along all lobes of the PLS.

Considering common aroma descriptors in the literature for individual pure compounds, similarities and overlaps are common within chemical classes. It is common for terpenic compounds to have aroma characteristics that include some subset of woody,

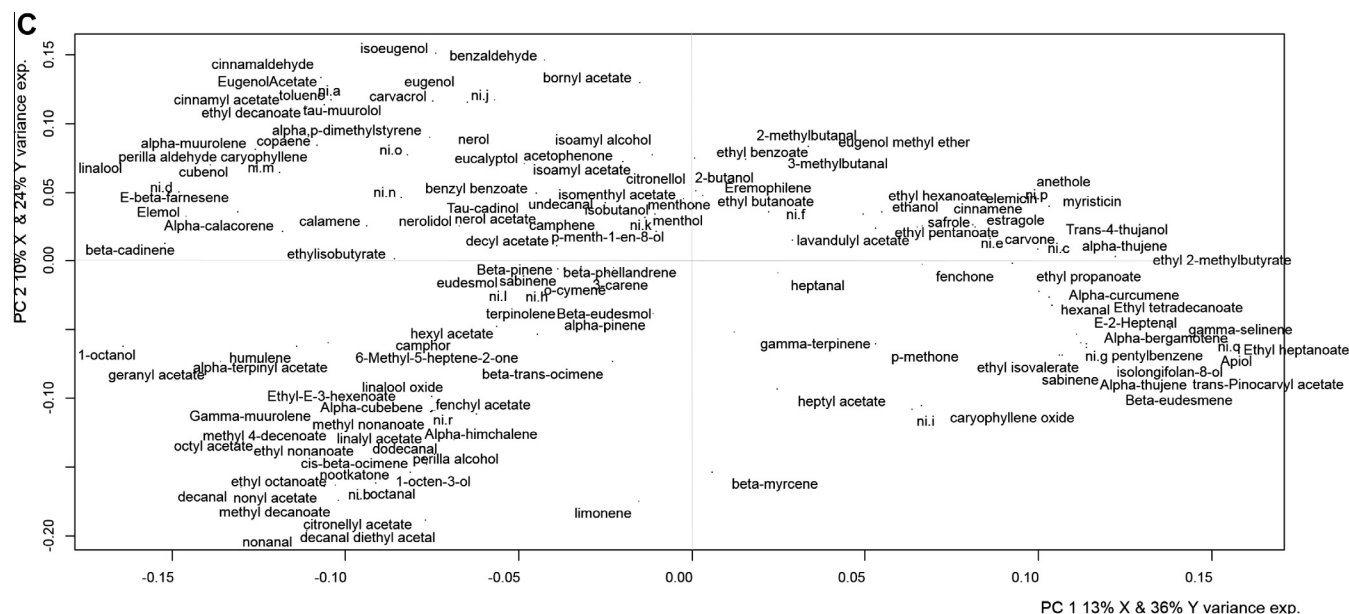


Fig. 2 (continued)

citrus, floral, herbal, spicy, and green; for example, citronellyl acetate has floral, rosy, green, fatty, woody, tropical fruit, aldehydic, and citrus characteristics; linalool has citrus, orange, green, woody, aldehydic, floral, terpy, and waxy characteristics; and beta-pinene has fresh, green, piney, woody, hay-like, terpy, minty, spicy, and resinous characteristics (All descriptors from Luebke, 2014, Perflavory). In this particular dataset, however, these compounds are each associated with three different, distant areas of the PLS, despite their aroma similarities as pure standards—citronellyl acetate with the citrus bitters and *orange candy* descriptor; linalool with the higher-variance aromatic bitters and the *cola* and *cinnamon* descriptors; and beta-pinene with the lower-variance aromatic and citrus bitters and the aroma descriptors *ginger*, *cardamom*, *juniper*, and *soapy*. Being built from rearrangements of 5-carbon isoprene units, different terpenic compounds will often share structural similarities with each other, which may be the source of the shared sensory characteristics these compounds have when isolated. That these compounds contribute differently to different sensory qualities, or have different aspects of their own sensory qualities emphasized, may have to do with concentration effects or synergistic or masking effects. These make straightforward sensory contributions more difficult to predict, and especially so in samples whose analysis is novel and therefore have fewer previous studies to be compared to. Pinpointing the direct relationship between volatiles that have similar and overlapping but not identical smells and the characteristic notes of the mixture remains a challenge. For example, why does the citrus aroma of citronellyl acetate lead to its correlation to citrus-like aromas in these samples, and not the citrusy aroma qualities of linalool? Novel sensory or psychophysical approaches may be necessary for determining which specific qualities of molecules are emphasized in a particular mixture, and how mixing affects the aroma contribution of a particular molecule in different situations. Chida et al. used cross-matching tests and correspondence analysis to determine which citrus-related compounds were more representative of lemon, orange, and sudachi fruits (Chida, Yamashita, Izumiya, Watanabe, & Tamura, 2006); in some cases, the most representative compounds for each fruit were only present in that fruit, such as citral in lemons; in other cases, compounds which sensorially were particularly representative for one type of fruit were present in all three fruits, such as alpha-pinene for sudachi aroma, or linalool for orange. Again, characteristic qualities of these plants or products

may have a significant contribution from mixing effects, as well (Francis & Newton, 2005; Johnson, Hirson, & Ebeler, 2012).

Generally, in complex mixtures such as these bitters and others of culinary interest, understanding how multiple compounds contribute to the overall aroma perception of the mixture, and which of these effects dominate across multiple samples is of greater import and value than only identifying the specific aromas of individual compounds, as would be more precisely elucidated with traditional GC-Olfactometry. Since the PLS reveals correlative rather than causative relationships, the correlative data discussed above for terpenic compounds could be showing that one or more of these compounds are highly associated with a particular descriptor or descriptors just by virtue of being present in a sample that is perceived to be high in the quality described by that descriptor, without necessarily acting as an impact compound for that descriptor. Conversely, the PLS may reveal real mixing-dependent perceptual effects where certain aspects of the multifaceted aroma of any one compound may be emphasized above the others, which could be masked depending on the other aroma qualities, or other types of compounds (aldehydes, phenylpropenoids), present.

### 3.4. Flavor chemistry of bitters

This study is the first attempt to characterize the flavor chemistry of cocktail bitters, an historically and gastronomically important product with complex volatile chemistry. 16 bitters samples of six different styles were found to have a well-differentiated range of 29 significantly different aroma characteristics by sensory analysis, and a total of 148 volatiles across many classes of natural products, some varying by up to three orders of magnitude across the set. Additionally, multivariate statistical analysis was able to predict 60% of the variance in the sensory characteristics in two dimensions with 23% of the variance in volatiles. In a creative context, the chemical and sensory dataset could have interdisciplinary benefits as well, providing new information about a product class widely used by chefs and bartenders that could complement their professional, intuitive knowledge of flavor and guide suggestions for further research questions. Additionally, the PCA and PLS, showing latent correlations both positive and negative, reveal unexplored flavor combinations – a bitters high in negatively correlated aromas, such as *green* and *ginger* or *chocolate* and *grapefruit*;

or high in an aroma character with low variance, such as *black pepper*, could be developed as a creative exercise directly inspired by this dataset. As discussed above, there are several unresolved questions relating to aroma and chemistry that impact both the present study specifically and broader understanding of flavor more theoretically and generally. One of these is why and how volatile molecules have several different aroma qualities (Chastrette, Elmouaffek, & Sauvegrain, 1988), and the structure-perception relationships and mechanisms by which this phenomenon occurs (Haddad et al., 2010; Hann, Leach, & Harper, 2001; Hendrickson, Huang, & Toczko, 1987; Kermen et al., 2011; Zarzo, 2011). How these effects integrate and interact to determine the perceived aroma of complex mixtures is a further question with great import to real-world flavor perception (Bushdid, Magnasco, Vosshall, & Keller, 2014; Jinks & Laing, 2001; Teixeira, Rodríguez, & Rodrigues, 2010).

Understanding these properties, both in a mechanistic context and in the context of what humans choose to eat for pleasure, will require continued use and further development of instrumental and statistical tools, as well as more comprehensive analysis of products of gastronomic interest which have not been addressed in the flavor chemistry literature. As alcoholic extractions of mixtures of aromatic plants, bitters are similar to gin, absinthe, chartreuse, or vermouth within the category of alcoholic beverages. All of these products are gastronomically important, chemically and sensorially complex, and are affected by the volatile compositions of many species. This may present unique challenges compared to strategies employed for more commonly analyzed spirits such as brandy or whiskey, which have volatile compositions and flavors tied to interactions between grapes or grain and yeast, and oak wood barrels and heat, rather than up to several dozen botanical species. Like bitters, these products' flavor chemistry have not been extensively analyzed. Gin has had some sensory and volatile profiling performed (Riu-Aumatell, Vichi, Mora-Pons, López-Tamames, & Buxaderas, 2008; Sanchez, 2011), and absinthe has been the subject of some chemical analysis that has mostly focused on quantifying concentrations of thujone and a few other components from wormwood (Lachenmeier, 2007; Lachenmeier et al., 2008). Vermouth, chartreuse, and other blended-aromatic-plant-based alcohol such as Campari have not been the subject of any published volatile or sensory studies that the authors have identified. Characterizing the flavor and volatile spaces and interrelationships of commercial versions of these products can guide further investigation into flavor development during extraction and distillation phases of production, and experiments characterizing their contributions to craft cocktails and other culinary situations.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2015.01.114>.

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