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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.

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 μL 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 μg/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 μm 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 μg/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 μL bitters in 20 mL deionized water in opaque black wineglasses. 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[a]	Dr. Adam Elmegirab	Aromatic	BOKERS	A1
Angostura Bitters[b]	Angostura	Aromatic	ANGOSTURA	A2
Jerry Thomas' Own Decanter Bitters[c]	Bitter Truth	Aromatic	JTDECANTER	A3
Whiskey Barrel-Aged Bitters	Fee Brothers	Aromatic	WHISKEY BARREL-AGED	A4
Regan's Orange Bitters Number 6[d]	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	XOCOLOTL 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[b]	Peychaud	New Orleans	PEYCHAUD	NO2
Orchard St Celery	Bittermen's	Celery	BMCELERY	C1
Celery Bitters	Scrappy's	Celery	SCRAPPYCELERY	C2

[a] Based on historical recipe for now-defunct Boker's brand.
[b] 9th century brand.
[c] Based on historical recipe from Jerry Thomas, The Bon Vivants Companion or How to Mix Drinks.
[d] 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.