CHARACTERIZATION OF VOLATILE COMPOUNDS IN QUALITY-RANKED GINS

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There is a large economic interest to characterize food products by objective analytical methods. This study characterized volatile compounds in different gins. Headspace Solid Phase Micro Extraction coupled with Gas Chromatography-Olfactometry Analysis identified 67 odorants in ten commercially available gins. 69 % of the odorants were identified as mono- and sesquiterpenes, representing phytochemicals of juniper berries and other plants. Furthermore, this study quantified 19 volatile compounds in gins of different sensory quality ranks. Principal Component Analysis identified six major gin compounds (MGC) with the highest effect on data variance. MGC contained monoterpenes β-pinene, γ-terpinene, limonene, ρ-cymene, β-myrcene and sabinene. Quantity ratios of each MGC were determined as percentage of total MGC concentration. MGC ratios of limonene, β-pinene and γ-terpinene showed significant differences between sensorial gold- and bronze-ranked gins. Gold-ranked gins showed MGC ratios of 27.4 ± 10.3 % limonene, 12.4 ± 4.5 % β-pinene and 9.7 ± 2.0 % γ-terpinene. Bronze-ranked gins showed MGC ratios of 55.5 ± 20.8 % limonene. Results indicated that the analyzed bronze-ranked gins had increased limonene quantity ratios compared to the gold-ranked gins. This investigation presents for the first time analytical differences between quality-ranked gins and may contribute to further studies on gin analytics.
Keywords: juniper, spirit drink, alcoholic beverage, GC-MS-O, quantity ratio

Charakterisierung flüchtiger Verbindungen in Gins von unterschiedlicher sensorischer Qualität.
Es besteht ein hohes wirtschaftliches Interesse daran, Lebensmittelprodukte durch objektive Analysemethoden zu beschreiben. Diese Studie charakterisiert flüchtige Verbindungen in zehn verschiedenen Gins. Durch Festphasenmikroextraktion und anschließender Analyse durch Gaschromatographie mit Olfaktometrie-Port wurden 67 Geruchsstoffe identifiziert. Davon wurden 69 % als Mono- und Sesquiterpene identifiziert, welche auch in sekundären Pflanzenstoffen von Wacholderbeeren und anderen Pflanzen vorhanden sind. Ferner wurden in dieser Studie 19 flüchtige Verbindungen in Gins mit unterschiedlicher sensorischer Qualität quantifiziert. Daraus wurden sechs Gin-Schlüsselverbindungen (GSV) mittels Hauptkomponentenanalyse identifiziert. Die GSV umfassten die Monoterpene β-Pinen, γ-Terpinen, Limonen, ρ-Cymol, β-Myrcen und Sabinen. Das prozentuale Mengenverhältnis jeder GSV zur gesamten GSV-Konzentration wurde bestimmt. Die GSV-Verhältnisse von Limonen, β-Pinen und γ-Terpinen zeigten signifikante Unterschiede zwischen Gins mit sensorischem Gold- und Bronze-Rang. Goldprämierte Gins zeigten die GSV-Verhältnisse 27,4 ± 10,3 % Limonen, 12,4 ± 4,5 % β-Pinen und 9,7 ± 2,0 % γ-Terpinen. Gins mit Bronze-Rang wiesen ein erhöhtes Limonen-Verhältnis von 55,5 ± 20,8 % auf. Die Studie zeigte zum ersten Mal analytische Unterschiede zwischen sensorisch bewerteten Gins auf und bietet die Basis für eine weiterführende Analytik von Gins.
Schlagwörter: Wacholder, Spirituose, alkoholisches Getränk, Gaschromatographie mit Olfaktometrie-Port, Mengenverhältnis

Gin is a spirit drink with long tradition in Europe dating back to the 17th century. The European Union defines gin as juniper-flavored spirit drink produced by flavoring ethyl alcohol of agricultural origin with juniper berries (*Juniperus communis* L.) (EU, 2019). Additional flavoring substances, in terms of different plant parts (botanicals), can be used to contribute to the aroma profile. All botanical ingredients contain phytochemicals, which are dissolved by ethanol-water maceration or steam infusion. Gin ingredient formulation often includes coriander seeds and citric fruits (Martin-Alvarez and Herranz, 1991). The composition of volatile and semivolatile compounds defines the sensory profile of the final gin product. EU regulation 2019/787, however, restricts the taste of gin predominantly to that of juniper. This provides a basis for quality-ranking gins by trained and certified judge panels as present in the German Agricultural Society (DLG). DLG provides objective quality control assessments in the food sector by descriptive sensory analyses and publishes ranking lists for gold-, silver- and bronze-ranked gins. DLG sensory analyses are performed by hedonic 5-points-scale schemes, rating anonymized products by optical, olfactory and taste attributes. Details on scheme attributes are, however, not published. In 2018 and 2019 84 DLG-ranked gins showed gold/silver/bronze ratios of 1.4/1.0/1.2 and 0.7/1.0/0.1, respectively (DLG, 2019). Gin has high potentials on the sales market and with 43 % showed the highest annual bottle sales increase from 2017 to 2018 in the spirits sector with finally 15.2 Mio. bottle (0.7 l) sales in Germany (BSI, 2019). There is a large economic interest in producing gold-ranked premium spirits and determining product quality-ranks by objective analytical methods. Although gin is a widely consumed spirit, analytical approaches to determine volatile compounds in gin and juniper-flavored spirit drinks are rare (Cardeal and Marriott, 2009; Martin-Alvarez and Herranz, 1991; Robbat et al., 2011; Sádecká et al., 2015; Vichi et al., 2005; Vichi et al., 2008). Approaches to identify compositional differences of sensorial ranked gins have not been conducted so far. In order to define gin on analytical level it is necessary to gain extensive information about its volatile composition. The aim of the presented study was (i) to identify volatiles in commercially available gins and (ii) to compare volatile compound quantities in bronze- and gold-ranked gins.

MATERIALS AND METHODS

GIN SAMPLES AND STANDARDS

Five DLG gold- (G1-5) and five DLG bronze-ranked (B1-5) gin samples (Table 1) were randomly chosen and ordered from commercial producers as published in DLG test results for spirit drinks (DLG, 2019). The sample size was based on limited availability of bronze-ranked gins. All samples were diluted with deionized water to gain ethanol concentrations of 37.5 % (v/v) for GC-Flame Ionization Detector (FID) analysis and 10 % (v/v) for headspace (HS)-Solid Phase Micro Extraction (SPME) Gas Chromatography-Olfactometry (GC-O) analysis. As gin aroma is defined by phytochemicals of different botanicals, gin samples were GC-FID analyzed for 19 volatile compounds found in juniper berries (Angioni et al., 2003; Carroll et al., 2011; Ghaly et al., 2016; Kallio and Jünger-Mannermaa, 1989; Marković et al., 2017; Robbat et al., 2011; Shahmir et al., 2003; Vichi et al., 2005), coriander (Anitescu et al., 1997) and citric fruits (Lin and Rouseff, 2001; Nardini et al., 2013). As literature implies, all quantified volatiles are aroma-active and are therefore referred to as aroma compounds. For aroma compound quantification, standard substances 2-undecanone, 4-thujanol, α-pinene, α-terpinyl acetate, β-myrcene, β-pinene, bornyl acetate, caryophyllene, citral, decanal, eucalyptol, limonene, linalool, octanal, ρ-cymene, sabinene, t-anethole and γ-terpinene were obtained from Merck KGaA (Darmstadt, Germany). Terpinen-4-ol was ordered from Carl Roth GmbH & Co.KG (Karlsruhe, Germany).

The gin samples were characterized for perceived odor aroma attributes in a descriptive manner. A trained judges panel of seven experienced assessors (age 24 to 48) received 40 ml (20 °C) of each gin in glass-lid covered spirit taster glasses. Every panelist individually smelled the sample and noted the attributes perceived. Subsequently, all attributes were collected and sorted for most attribute term repetitions to lowest. Only attribute terms with ≥ 2 repetitions were considered in Table 1.

Table 1: Gin sample set

no.	quality-rank	gin category	alc. %(v/v)	descriptive odor aroma attributes
B1	bronze	Gin	44.7	juniper, citrus, flat, orange, effervescent, fruit gum, herbs, floral, pungent, lime, mild, woodruff
B2	bronze	London Dry Gin	43.1	juniper, citrus, allspice, liquorice, orange, spicy, woody, angelica root, anise, eucalyptus, fresh, herbs, mint, essential oils, sweet, vegetal
B3	bronze	Distilled Dry Gin	44.1	juniper, citrus, black pepper, cardamom, anise, coriander, flat, herbs, leather, liquorice, musty, orange, soapy, spicy, sweet, wet soil, woody
B4	bronze	London Dry Gin	37.5	juniper, citrus, floral, herbs, flat, clean, fresh, soapy, vegetal
B5	bronze	Gin	41.8	orange, soapy, juniper, citrus, coriander, floral, fresh, lavender, cinnamon, fatty, fruity, ginger, liquorice, metallic, rosemary
G1	gold	Gin	41.9	juniper, floral, orange, citrus, spicy, angelica root, apple, cinnamon, clove, coriander, essential oils, fruity, ginger, lavender, pine, resin, spicy, tarragon, vegetal, rose
G2	gold	Dry Gin	40.9	juniper, citrus, flat, floral, fruity, ginger, lavender, orange, soapy, soft, sweet, vegetal
G3	gold	London Dry Gin	42.0	juniper, citrus, floral, orange, spicy, allspice, clove, coriander, effervescent, ginger, herbs, lavender, pine, southernwood, vegetal
G4	gold	Gin	45.2	juniper, citrus, black pepper, fruity, alcoholic, apple, complex, fresh, fruity, pine, plum, raisin, vegetal, woody
G5	gold	Dry Gin	41.8	juniper, citrus, orange, herbs, complex, coriander, floral, fresh, fruit gum, fruity, lavender, lime, mango, pine, spicy, vegetal

HS-SPME SAMPLING

For identification of odorants, all gins were sampled with HS-SPME method, based on ideal conditions described by Vichi et al. (2005). Prior to sampling, a 50/30 µm DVB/CAR/PDMS SPME fiber (Supelco, Bellefonte, USA) with 24 ga needle was conditioned for 30 min at 300 °C in an SPME arrow conditioning station (Gerstel, Mülheim an der Ruhr, Germany) to prevent contamination. Sampling was conducted with sample volumes of 2.5 ml placed in a 10 ml vial with silicone septum. The samples were water-bath heated to 50 °C and stirred at 250 rpm with a magnetic stir bar. SPME headspace extraction time was set to 30 min.

GC-MS-O ANALYSIS

After SPME, the analytes were directly released to a gas chromatography system equipped with a mass spectrometric detector and an olfactory detection port system. Analyses were performed on a 7890B gas chromatograph, coupled to a single quadrupole 5877B MS detection system from Agilent Technologies (Santa Clara, USA), equipped with thermal desorption unit TDU2, cooled injection system CIS, olfactory detector port ODP 3 and olfactory intensity device OID 1 from Gerstel (Mülheim an der Ruhr, Germany). Fiber-extracted aroma compounds were thermally desorbed in the TDU unit at initially 40 °C for 1 min and increased to 240 °C for 5 min. The subsequent CIS unit cryofocused and reheated the compounds to 240 °C for 5 min before column injection. Volatiles were carried by helium stream (1.62 ml/min) to the 30 m × 0.25 mm × 0.25 µm polar DB-WAX column (122-7032UI, Agilent Technologies, Santa Clara, USA). GC analysis was carried out at 40 °C (3 min) with temperature increase rate of 5 °C/min to reach 240 °C (5 min). The gas flow was split at a ratio of 1:1 to enter the MS detector and the ODP. The following parameters were applied: MS mode, scan; scan range, m/z 33 to 330; electron ionization energy, 70 eV; source temperature, 230 °C; quadrupole temperature, 150 °C, ODP 3 makeup gas, N2 (5.0, Linde, Munich, Germany). Two trained persons (male, 24 to 25 years, 2nd year students of master's program food science and engineering, specialized on aroma investigation in spirit drinks) identified the odor impressions in the GC-MS-O experiments. For compound identification, all detected odorants were analyzed for retention indices and mass spectra. Firstly, retention indices were determined with reference to a homologous standard series of C9 to C30 hydrocarbons. All compounds were compared to reference mass spectra of the National Institute of Standards and Technology (NIST) MS database (MassHunter, Agilent Technologies, Santa Clara, USA). Secondly, all compounds matching the NIST-database (match factor >75 %) were tentatively identified by Kovats retention indices (KI) (Ettre, 1993) (tolerance ± 20) available in literature (Fan and Qian, 2005; Ferrari et al., 2004; Goodner, 2008; Ledauphin et al., 2004; Salinas et al., 2004; Vichi et al., 2005; Zhao et al., 2009) and database sets (Nist,2020; Nlm,2020; The Pherobase, 2020).

GC-FID ANALYSIS

The GC-FID method is recommended for the quantification of volatile congeners in spirit drinks (Kelly et al; 1999). For GC-FID analyses a GC-2010 system, equipped with a HS-20 headspace sampler from Shimadzu (Shimadzu Deutschland GmbH, Duisburg, Germany) was used with 60.0 m × 0.32 mm × 1,5 µm rtx-volatiles column (Restek Corp., Bellefonte, USA). The temperature program was set as follows: 60 °C (2 min), ramped at 12.5 °C/min to 160 °C (2 min) and then ramped at 12.5 °C/min to 250 °C (10 min). All 19 standards were five-point calibrated ($R^2 \geq 0.95$) in concentration range of 0.1 to 4.0 mg/l (0.1, 0.2, 1.0, 2.0, 4.0 mg/l). The limit of quantification (LOQ) was 0.1 mg/l. All gin samples were analyzed in triplicate.

STATISTICAL EVALUATION

Principal Component Analysis (PCA) was performed with statistical analysis software SPSS 25 (IBM Corp., Armonk, USA) to identify major gin compounds (MGC). Quantity ratios (QR) of all identified compounds were calculated as percentage of total MGC concentration in every gin sample. Parametric free Kruskal-Wallis test was applied to identify significant differences ($p < 0.05$) between bronze- and gold-ranked gins.

RESULTS AND DISCUSSION

IDENTIFICATION OF ODORANT ACTIVE COMPOUNDS

The GC-MS-O analysis of ten gins identified a total of 67 compounds. The tentatively identified volatile compounds are shown in Tables 2a, 2b and 2c. In total, the detected odorants comprised to 69 % of mono- and sesquiterpenic hydrocarbons in their oxygenated and non-oxygenated derivates. Our results overlap the terpene identification of Vichi et al. (2005) to 75 %. The identified monoterpenes included α-pinene, β-pinene, sabinene, β-myrcene, β-phellandrene, ρ-cymene and terpinolene, representing typical juniper berry extract composition (Angioni et al., 2003; Kallio and Jünger-Mannermaa, 1989; Shahmir et al., 2003). Surprisingly, limonene as a characteristic monoterpene gin

compound (Martin-Alvarez and Herranz, 1991; Robbat et al., 2011) was not detected via GC-MS-O analysis. This might be due to olfactory overlaps with other volatile compounds. In literature, limonene has been described with close retention times to eucalyptol (Robbat et al., 2011; Vichi et al., 2005) and therefore tends to have similar volatility characteristics. In our investigation, the odor impression of eucalyptol at the olfactory detector port was described with the olfactory attributes *wood* and *citrus*, which might resemble an overlap with limonene.

18 sesquiterpenes were identified of which 15 have already been described in juniper berry extracts (Angioni et al., 2003; Carroll et al., 2011; Kallio and Jünger-Mannermaa, 1989; Marković et al., 2017; Shahmir et al., 2003; Vichi et al., 2005). The sesquiterpenes β-patchoulene, nerolidol and β-sinensal have been described as characteristic for other plant extracts from e. g. patchouli (Hu et al., 2006), cypress (Kallio and Jünger-Mannermaa, 1989) and grapefruit (Lin and Rouseff, 2001). In total, 14 oxygenated monoterpenes were detected in the gin samples of which 12 have also been described in juniper berry extracts (Angioni et al., 2003; Carroll et al., 2011; Kallio and Jünger-Mannermaa,1989; Marković et al., 2017; Shahmir et al., 2003; Vichi et al., 2005). For the other oxygenated monoterpenes, neral has been described in coriander extracts (Anitescu et al., 1997) while citral is a double bond of the isomers geranial and neral and related to citrus fruits (Nardini et al., 2013). Also most detected oxygenated sesquiterpenes can be linked to juniper berries (Angioni et al., 2003; Carroll et al., 2011; Shahmir et al., 2003; Vichi et al., 2005), whereas junenol and epicubenol occur in other plant extracts of e. g. cypress (Carrol et al., 2011) and betel (Thanh et al., 1997). The gin samples also contained esters of which linalyl acetate and neryl acetate can be linked to juniper berries (Angioni et al., 2003; Vichi et al., 2005). Hexyl tiglate and chrysanthenyl acetate have been identified in components of green leaves (Rutter, 2000) and plant parts of *Tanacetum parthenium* (Rateb et al., 2007). The identified phenolic substances anethole, estragole and eugenol occur in different plants of the family *Apiaceae*, e. g. coriander or fennel (Anitescu et al., 1997; Raffo et al., 2011). Nonanal aldehydes and 2-undecanone ketones have also been detected in juniper berry extracts (Vichi et al., 2005). Overall, the identified odorants showed a close relation to phytochemicals of mainly juniper berries and other plants, as expected for the process step of gin production.

QUANTIFICATION OF MAJOR GIN DEFINING COMPOUNDS

19 volatile compounds were quantified in ten gin samples (Table 3). Caryophyllen oxide, decanal and 2-undecanone were detected below LOQ and therefore not further considered for evaluation. The results showed that the analyzed gins differed in their aroma compound compositions. For instance, monoterpenes α-pinene, β-pinene, sabinen, β-myrcene, limonene, ρ-cymene and γ-terpinene were present in wide concentration ranges of < 0.1 to 31.87 mg/l and can be linked to juniper berry extracts (Angioni et al., 2003; Kallio and Jünger-Mannermaa,1989; Shahmir et al., 2003). Vichi et al. (2005) found comparable monoterpenic concentrations in different gins. The highest concentrations of α-pinene and β-myrcene were found in G5. B5 contained the highest concentrations of terpinen-4-ol and anethole. This is probably due to infusion of *Apiaceae* fruits, e. g. coriander (Anitescu et al., 1997; Raffo et al., 2011), during gin production. On average, linalool was the most abundant compound among all gin samples with an average concentration of 14.2 ± 12.8 mg/l. Linalool occurs in traces in juniper berries but dominates the aroma compounds of coriander oil (Anitescu et al., 1997). This indicated that coriander seemed to be an abundant botanical in the analyzed gins. PCA on quantified chemical compounds gave two major factors (PC1, PC2) with captured variance of 47.0 % for PC1 and 29.2 % for PC2. Factor PC1 was mainly influenced by monoterpenes β-pinene, γ-terpinene, limonene, ρ-cymene, β-myrcene and sabinene with loading factors > 0.83 (Fig. 1). These six monoterpenes had the highest influence on data variance of bronze- and gold-ranked gins and were therefore identified as MGC of the data set. PCA further indicated that monoterpenes α-pinene and linalool had lower importance on data variance with a loading factor of 0.76.

Table 2a: Gin volatiles tentatively identified by GC-MS-O analysis with determined Kovats Index on DB-Wax Column

no.	chemical substance	odor impression	CAS[a]	RT	KI (DB-Wax)
	monoterpenes				
1	α-pinene	resin, wood	80-56-8	5.61	1010
2	β-pinene	pine	18172-67-3	7.39	1081
3	sabinene	wood, turpentine	3387-41-5	7.68	1093
4	β-myrcene	spice	123-35-3	8.68	1134
5	β-phellandrene	mint, turpentine	555-10-2	9.55	1165
6	p-cymene	lemon	535-77-3	11.14	1226
7	terpinolene	herb	586-62-9	11.33	1237
	sesquiterpenes				
8	α-cubebene	herb	17699-14-8	16.14	1408
9	β-patchoulene	n.d.	514-51-2	18.39	1497
10	β-elemene	n.d.	515-13-9	19.77	1562
11	γ-elemene	wood	3242-08-8	20.76	1612
12	α-caryophyllene and	spice, wood	6753-98-6	21.75	1646
13	germacrene D	herb, spice	317819-80-0	22.10	1670
14	γ-muurolene	wood	30021-74-0	22.21	1660
15	β-bisabolene	n.d.	495-61-4	23.17	1700
16	β-selinene	herb	17066-67-0	23.17	1700
17	δ-cadinene	wood, herb	483-76-1	23.82	1737
18	β-cadinene	n.d.	523-47-7	23.95	1740
19	*c*-calamenene	n.d.	72937-55-4	25.28	1793
20	germacrene B	wood	15423-57-1	25.33	1801
21	α-calacorene	wood	21391-99-1	27.08	1886
22	humulene-1,2-epoxide	resin	19888-34-7	29.49	2011
23	(E)-nerolidol	n.d.	40716-66-3	29.60	2022
24	β-sinensal	citrus	60066-88-8	32.97	2201

Table 2b: Gin volatiles tentatively identified by GC-MS-O analysis with determined Kovats Index on DB-Wax Column

no.	chemical substance	odor impression	CAS[a]	RT	KI (DB-Wax)
25	α-cadinol	herbs	481-34-5	33.12	2210
	oxygenated monoterpenes				
26	eucalyptol	wood, citric	470-82-6	9.98	1178
27	rose oxide L	floral	16409-43-1	13.64	1312
28	α-campholenal	herbs	4501-58-0	17.37	1463
29	linalool	floral	78-70-6	19.09	1535
30	bornyl acetate	melon, resin	76-49-3	19.67	1561
31	terpinen-4-ol	spice	562-74-3	20.35	1585
32	*t*-pinocarveol	floral	547-61-5	21.57	1637
33	neral	n.d.	106-26-3	22.06	1652
34	α-terpinyl acetate	herbs	80-26-2	22.42	1677
	oxygenated monoterpenes				
35	α-terpineol	floral	10482-56-1	22.54	1680
36	neryl acetate	n.d.	141-12-8	23.09	1703
37	citral	lemon, fresh, citrus	5392-40-5	23.21	1709
38	geranyl acetate	floral	105-87-3	23.76	1734
39	nerol	floral	106-25-2	24.75	1782
40	geraniol	floral	106-24-1	25.74	1817
	oxygenated sesquiterpenes				
41	caryophyllene oxide	nut, honey	1139-30-6	28.44	1958
42	junenol	n.d.	472-07-1	29.88	2032
43	epicubenol	n.d.	19912-67-5	30.07	2038
44	elemol	wood	639-99-6	30.37	2060
45	τ-cadinol	soil	5937-11-1	31.97	2149
46	τ-muurolol	herb	19912-62-0	32.30	2165

Table 2c: Gin volatiles tentatively identified by GC-MS-O analysis with determined Kovats Index on DB-Wax Column

no.	chemical substance	odor impression	CAS[a]	RT	KI (DB-Wax)
	esters				
47	ethyl octanoate	fruit	106-32-1	16.07	1416
48	*t*-chrysanthenyl acetate	n.d.	50764-55-1	18.26	1492
49	ethyl nonaoate	fruit	123-29-5	18.62	1512
50	linalyl acetate	n.d.	115-95-7	19.06	1525
51	hexyl tiglate	n.d.	16930-96-4	20.74	1600
52	ethyl decanoate	fruit	110-38-3	21.16	1629
53	ethyl benzoate	fruit	93-89-0	21.60	1633
54	ethyl *t*-*c*-2,4-	fruit	3025-30-7	25.71	1825
55	ethyl dodecanoate	fruit	106-33-2	25.79	1831
56	diethyl phthalate	ruber	84-66-2	35.27	2334
	alcohols, aldehydes, ketones, phenoles				
57	ethanol	alcohol	64-17-5	4.31	932
58	octanal	citrus, fresh	124-13-0	12.04	1261
59	nonanal	citrus, lemon	124-19-6	14.92	1365
60	decanal	citrus, fresh	112-31-2	17.58	1460
61	2-undecanone	fruit	112-12-9	20.16	1567
62	estragole	anise	140-67-0	23.59	1635
63	(Z)-anethole	anise, fresh	104-46-1	25.15	1794
64	(2E)-3-phenylprop-2-	cinnamon	57194-69-1	26.39	1853
65	methyleugenol	n.d.	93-15-2	28.96	1985
66	eugenol	n.d.	97-53-0	31.74	2133
67	2,4-di-tert-butylphenol	phenol	96-76-4	34.38	2282

[a] Chemical abstracts service; n.d. = not defined

Table 3: Quantified volatiles in gins of different quality-ranks

	mean concentration (mg/l)									
	B1[a]	**B2[a]**	**B3[a]**	**B4[a]**	**B5[a]**	**G1[b]**	**G2[b]**	**G3[b]**	**G4[b]**	**G5[b]**
α-pinene	2.00	1.35	6.38	0.26	<LOQ	1.07	0.49	8.8	<LOQ	31.87
β-pinene	<LOQ	2.60	1.80	<LOQ	<LOQ	0.44	0.36	1.26	0.30	1.75
sabinene	0.86	3.85	2.54	<LOQ	0.51	0.82	0.69	1.62	0.27	0.70
β-myrcene	1.12	10.74	2.19	0.36	0.59	0.77	0.46	2.72	0.13	10.94
limonene	4.44	7.28	8.33	1.28	2.61	1.28	0.25	4.99	0.41	7.63
p-cymene	<LOQ	3.04	1.68	<LOQ	0.39	0.50	0.17	1.08	0.38	0.88
γ-terpinene	<LOQ	2.51	0.96	<LOQ	0.35	0.48	0.21	1.11	0.20	1.64
eucalyptol	0.36	<LOQ	3.99	<LOQ	1.45	0.70	0.22	2.57	<LOQ	0.15
linalool	4.71	21.08	11.21	1.58	11.12	17.22	2.56	39.22	2.57	30.27
terpinen-4-ol	6.62	12.27	3.59	2.60	34.02	14.79	5.51	5.42	7.87	4.05
α-terpinyl acetate	0.16	<LOQ	2.45	<LOQ	0.23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
anethole	<LOQ	6.13	<LOQ	<LOQ	21.56	<LOQ	<LOQ	<LOQ	<LOQ	0.28
4-thujanol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.32	<LOQ
bornyl acetate	<LOQ	0.13	<LOQ	<LOQ	0.48	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
citral	1.45	3.57	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
octanal	<LOQ	<LOQ	<LOQ	<LOQ	0.24	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

[a] bronze-ranked gin; [b] gold-ranked gin; LOQ = limit of quantification < 0.1 mg/l

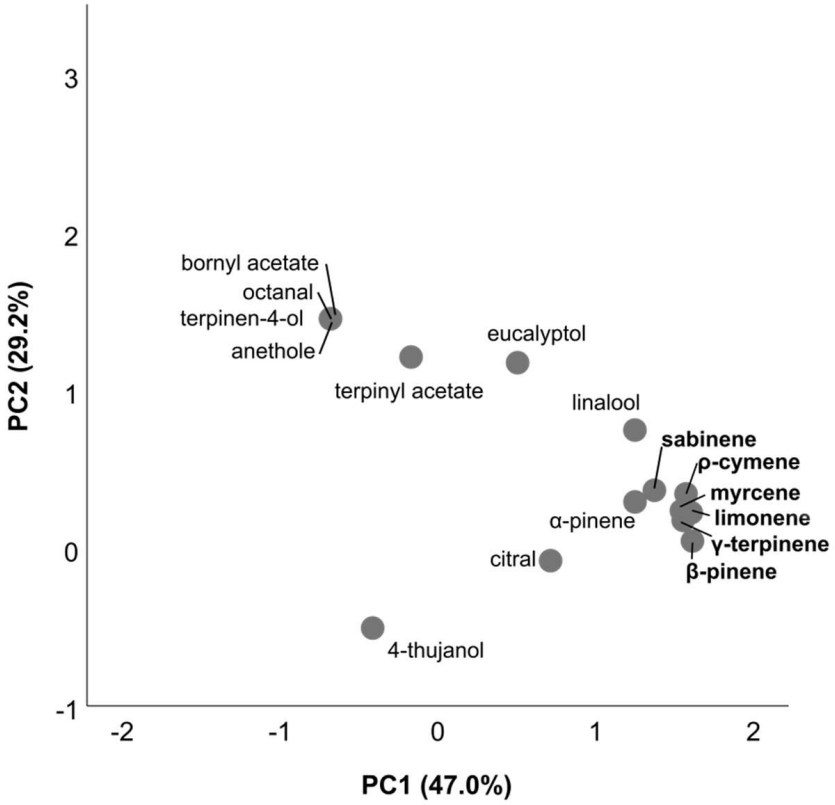

Fig. 1: Principal component analysis of analyzed volatiles in quality-ranked gins with identified major gin compounds (bold)

QUANTITY RATIOS OF MAJOR GIN QUALITY COMPOUNDS

The cumulated MGC concentrations in gins ranged from 1.6 to 30.0 mg/l. Single volatile compound concentrations did not show significant differences between bronze- and gold-ranked gins. On average, QR analysis determined limonene with the highest share of 41.5 ± 21.4 % on total MGC. QR of limonene, β-pinene and γ-terpinene showed significant differences between bronze- and gold-ranked gins (Fig. 2). Furthermore, it showed that the analyzed bronze-ranked gins had significantly higher limonene ratios, while gold-ranked gins had significantly higher shares of β-pinene and γ-terpinene. Gold-ranked gins were identified with average QR of 27.4 ± 10.3 % limonene, 12.4 ± 4.5 % β-pinene and 9.7 ± 2.0 % γ-terpinene. Bronze-ranked gins showed MGC ratios of 55.5 ± 20.8 % limonene. This indicated that the analyzed gins showed different QR in respect to their quality rank. Limonene is a major compound in citric fruits and sensorial characterized as *citrusy*, *fresh* and *licorice*, while β-pinene and γ-terpinene are referred to as *musty*, *green*, *resinous*, *lemon* or *terpeny* (Högnadóttir and Rouseff, 2003; Riu-Aumatel et al., 2008). Riu-Aumatel et al. (2008) defined five major sensory descriptors for gins with juniper, citric, licorice, aniseed and spice. In fact, they showed a close relation between sensory characteristics and specific volatile compounds. Limonene was related to perceived citric notes in gins. In combination with our results it seems that the analyzed gins with reduced limonene ratios and, in terms, reduced citric aroma notes characterize the analyzed gold-rank.

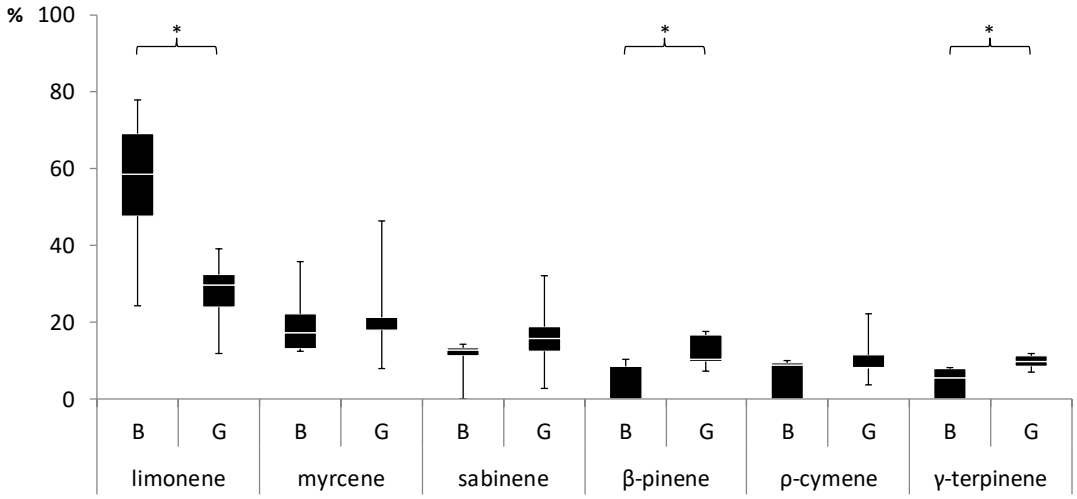

Fig. 2: Quantity ratios of six major gin compounds in (B) bronze- and (G) gold-ranked gins (n = 5); asterisks indicate significant differences ($p < 0.05$)

CONCLUSION

In this work, gins of different sensory qualities were analyzed for their volatile composition. Data of the presented investigation indicate, that differences in sensorial perceived quality-ranks were definable with determination of MGC and QR analysis. Taking into account that single volatile compound concentrations did not show significant differences between gin quality ranks, the introduction of MGC and QR might open possibilities to define quality-rank differences. These findings may contribute to further studies on gin quality analysis.

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REFERENCES

Angioni, A., Barra, A., Russo, M. T., Coroneo, V., Dessí, S. and Cabras, P. 2003: Chemical composition of the essential oils of Juniperus from ripe and unripe berries and leaves and their antimicrobial activity. Journal of Agricultural and Food Chemistry 51: 3073-3080. https://doi.org/10.1021/jf026203j

Anitescu, G., Doneanu, C. and Radulescu, V. 1997: Isolation of Coriander Oil: Comparison Between Steam Distillation and Supercritical CO2 Extraction. Flavour and Fragrance Journal 12: 173-176. https://doi.org/10.1002/(SICI)1099-1026(199705)12:3<173::AID-FFJ630>3.0.CO;2-1

BSI. 2019: Spirituosen-Hitparade im LEH 2017/2018 in Gesamtdeutschland (Flaschen). In: BSI (Hrsg.): Daten aus der Alkoholwirtschaft. Bonn: Bundesverband der Deutschen Spirituosen-Industrie und -Importeure e. V. (BSI), 2019

Cardeal, Z. L. and Marriott, P. J. 2009: Comprehensive two-dimensional gas chromatography–mass spectrometry analysis and comparison of volatile organic compounds in Brazilian cachaça and selected spirits. Food Chemistry 112: 747–755. https://doi.org/10.1016/j.foodchem.2008.06.057

Carroll, J. F., Tabanca, N., Kramer, M., Elejalde, M. E., Wedge, D. E., Bernier, U. R., Coy, M., Becnel, J. J., Demirci, B., Başer, K. H. C., Zhang, J. and Zhang, S. 2011: Essential oils of Cupressus funebris, Juniperus communis, and J. chinensis (Cupressaceae) as repellents against ticks (Acari: Ixodidae) and mosquitoes (Diptera: Culicidae) and as toxicants against mosquitoes. Journal of Vector Ecology 36: 258-268. https://doi.org/10.1111/j.1948-7134.2011.00166.x

Dlg. 2019: Testergebnisse Spirituosen - Deutsche Landwirtschaftsgesellschaft DLG. http://dlg-verbraucher.info. (23.10.2019)

Ettre, L. S. 1993: Nomenclature for chromatography. Pure and Applied Chemistry 64: 819–872. https://doi.org/10.1351/pac199365040819

Eu. 2019: Regulation (EU) 2019/787. Brussels: Official Journal of the European Union 130

Fan, W. and Qian, M. C. 2005: Headspace solid phase microextraction and gas chromatography-olfactometry dilution analysis of young and aged Chinese "Yanghe Daqu" liquors. Journal of Agricultural and Food Chemistry 53: 7931–7938. https://doi.org/10.1021/jf051011k

Ferrari. G., Lablanquie, O., Cantagrel, R., Ledauphin, H., Payot, T., Fournier, N. and Guichard, E. 2004: Determination of key odorant compounds in freshly distilled Cognac using GC-O, GC-MS, and sensory evaluation. Journal of Agricultural and Food Chemistry 52: 5670–5676. https://doi.org/10.1021/jf049512d

Ghaly, N. S., Mina, S. A. and Younis, N. 2016: Schistosomicidal and molluscicidal activities of two Junipers species cultivated in Egypt and the chemical composition of their essential oils. Journal of Medicinal Plants Research 10: 47-53. https://doi.org/10.5897/JMPR2015.5993

Goodner, K. L. 2008: Practical retention index models of OV-101, DB-1, DB-5, and DB-Wax for flavor and fragrance compounds. Journal of Food Science and Technology 41: 951-958. https://doi.org/10.1016/j.lwt.2007.07.007

Högnadóttir, Á. and Rouseff, R. L. 2003: Identification of aroma active compounds in orange essence oil using gas chromatography–olfactometry and gas chromatography–mass spectrometry. Journal of Chromatography A 998: 201-211. https://doi.org/10.1016/S0021-9673(03)00524-7

Hu, L. F., Li, S. P., Cao, H., Liu, J. J., Gao, J. L., Yang, F. Q. and Wang, Y. T. 2006: GC–MS fingerprint of

Pogostemon cablin in China. Journal of Pharmaceutical and Biomedical Analysis 42: 200-206. https://doi.org/10.1016/j.jpba.2005.09.015

Kallio, H. and Jünger-Mannermaa, K. 1989: Maritime influence on the volatile terpenes in the berries of different ecotypes of juniper (Juniperus communis L.) in Finland. Journal of Agricultural and Food Chemistry 37: 1013-1016. https://doi.org/10.1021/jf00088a043

Kelly, J., Chapman, S., Brereton, P., Bertrand, A., Guillou, C. and Wittkowski, R. 1999: Gas Chromatographic Determination of Volatile Congeners in Spirit Drinks: Interlaboratory Study. Journal of AOAC International 82: 1375-1388. https://doi.org/10.1093/jaoac/82.6.1375

Ledauphin, J., Saint-Clair, J. F., Lablanquie, O., Guichard, H., Founier, N., Guichard, E. and Barillier, D. 2004: Identification of trace volatile compounds in freshly distilled calvados and cognac using preparative separations coupled with gas chromatography-mass spectrometry. Journal of Agricultural and Food Chemistry 52: 5124–34. https://doi.org/10.1021/jf040052y

Lin, J. and Rouseff, R. L. 2001: Characterization of aroma-impact compounds in cold-pressed grapefruit oil using time–intensity GC–olfactometry and GC–MS. Flavour and Fragrance Journal 16: 457–463. https://doi.org/10.1002/ffj.1041

Marković, M. S., Bošković-Vragolović, N. M., Ristić, M. S., Pavićević, V. P., Veljković, V. B. and Milojević, S. Ž. 2017: Fractionation of the essential oil from juniper (Juniperus communis L.) berries by hydrodistillation and rectification. Hemijska industrija 71: 471-477. https://doi.org/10.2298/HEMIND161204009M

Martin-Alvarez, P. J. and Herranz, A. 1991: Application of Multivariate Statistical Methods to the Differentiation of Gin Brands. Journal of the Science of Food and Agriculture 57: 263-272. https://doi.org/10.1002/jsfa.2740570210

Nardini, G. S., Merib, J.S., Dias, A. N., Dutra, J. N. B., Silveira, C. D. S, Budziak, D., Martendal, E. and Carasek, E. 2013: Determination of volatile profile of citrus fruit by HS-SPME/GC-MS with oxidized NiTi fibers using two temperatures in the same extraction procedure. Microchemical Journal 109: 128-133. https://doi.org/10.1016/j.microc.2012.03.024

Nist. 2020: NIST Chemistry Webbook - National Institute of Standards and Technology NIST. https://webbook.nist.gov/chemistry. (15.01.2020)

NLM. 2020: U.S. National Library of Medicine (NLM). https://pubchem.ncbi.nlm.nih.gov. (15.01.2020)

Raffo, A., Nicoli, S. and Leclercq, C. 2011: Quantification of estragole in fennel herbal teas: Implications on the assessment of dietary exposure to estragole. Food and Chemical Toxicology 49: 370-375. https://doi.org/10.1016/j.fct.2010.11.011

Rateb, M. E. M., El-Gendy, A-N. A. M., El-Hawary, S. S. and El-Shamy, A. M. 2007: Phytochemical and biological investigation of Tanacetum parthenium (L.) cultivated in Egypt. Journal of Medicinal Plants Research 1: 18-26.

Riu-Aumatel, M., Vichi, S., Mora-Pons, M., López-Tamames, E. and Buxaderas, S. 2008: Sensory Characterization of Dry Gins with Different Volatile Profiles. Journal of Food Science 73: 286-293. https://doi.org/10.1111/j.1750-3841.2008.00820.x

Robbat, J., Kowalsick, A. and Howell, A. 2011: Tracking juniper berry content in oils and distillates by spectral deconvolution of gas chromatography/mass spectrometry data. Journal of Chromatography A 1218: 5531–5541. https://doi.org/10.1016/j.chroma.2011.06.053

Ruther, J. 2000: Retention index database for identification of general green leaf volatiles in plants by coupled capillary gas chromatography– mass spectrometry. Journal of Chromatography A 890: 313-319. https://doi.org/10.1016/S0021-9673(00)00618-X

Sádecká, J., Uríčková, V., Hroboňová, K. and Májek, P. 2015: Classification of Juniper-Flavoured Spirit Drinks by Multivariate Analysis of Spectroscopic and Chromatographic Data. Food Analytical Methods 8: 58-69. https://doi.org/10.1007/s12161-014-9869-8

Salinas, M., Zalacain, A., Pardo, F. and Alonso, G. L. 2004: Stir bar sorptive extraction applied to volatile constituents evolution during Vitis vinifera ripening. Journal of Agricultural and Food Chemistry 52: 4821–4827. https://doi.org/10.1021/jf040040c

Shahmir, F., Ahmadi, L., Mirza, M. and Kororı, S. A. A. 2003: Secretory elements of needles, berries of Juniperus communis L. ssp. communis and its volatile constituents. Flavour and Fragrance Journal 18: 425-428. https://doi.org/10.1002/ffj.1243

Thanh, L., Dung, N. X., Bighelliand, A., Casanova, J. and Leclercq, P. A. 1997: Combination of capillary GC, GC/MS and 13C-NMR for the characterization of the rhizome oil of Piper betle L. (Piperaceae) from Vietnam. Spectroscopy 13:131-136. https://doi.org/10.1155/1997/397354

The Pherobase. 2020: http://www.pherobase.com. (15.01.2020)

Vichi, S., Riu-Aumatell, M., Buxaderas, S. and López-Tamames, E. 2008: Assessment of some diterpenoids in commercial distilled gin. Analytical Chimica Acta 628: 222–229. https://doi.org/10.1016/j.aca.2008.09.005

Vichi, S., Riu-Aumatell, M., Mora-Pons, M., Buxaderas, S. and Pez-Tamames, E. L. 2005: Characterization of volatiles in different dry gins. Journal of Agricultural and Food Chemistry 53: 10154–10160. https://doi.org/10.1021/jf058121b

Zhao, Y., Xu, Y., Li, J., Fan, W. and Jiang, W. 2009: Profile of Volatile Compounds in 11 Brandies by Headspace Solid-Phase Microextraction Followed by Gas Chromatography-Mass Spectrometry. Journal of Food Science 74: 90-99. https://doi.org/10.1111/j.1750-3841.2008.01029.x

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