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Characterization of Volatiles in Different Dry Gins

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A HS-SPME method coupled to GC-MS was developed and applied for the qualitative and semiquantitative characterization of distilled gin volatile fraction. Sampling, chromatographic conditions, and method performances were evaluated, and the developed method was applied as a comparative study of some of the most popular commercial London Dry Gins and other gins with geographic denominations. During this study, 70 components of the gins' volatile fraction were isolated, tentatively identified or identified by reference compounds. They were mainly represented by mono- and sesquiterpenic compounds, which were quantitatively determined. The comparative study of London Dry Gins and gins with geographical indication permitted clear differentiation between the gins with geographical indication and one of the London Dry Gins tested.

KEYWORDS: Gin; volatiles; characterization; SPME; geographical indication

INTRODUCTION

Gin is a distilled beverage developed in northern Europe in the 17th century. It has several classes and formulations. The most popular is London Dry Gin. According to European Union (EU) regulations (*1*), it belongs to the "Distilled gin" class, which is produced by redistillation of alcohol 96% (v/v) in the presence of juniper berries (*Juniperus communis*) and other natural, botanical ingredients such as coriander seeds, cardamom seeds, calamus root, angelica root (*2*), licorice root, orange peel, lemon peel, and anise seeds (*3*). All of these ingredients are rich in essential oils, which contribute to the aroma of most gins, but the main flavor of distilled gin should come from the juniper berries (*1*).

When the production process takes place within a specific geographical area and fulfills certain requirements concerning elaboration, composition, and quality, the gins can receive the denomination of geographical indication, as in the case of Plymouth gin (U.K.) and Mahon gin (Spain) (*1*).

Although gin is well-known and widely consumed, there are few documented studies on its composition and characteristics available (*2*, *4*, *5*). In these works, the presence of around 30 tentatively identified terpenic compounds was described in the volatile fraction of distilled gin after the performance of liquid−liquid extractions followed by gas chromatographic analysis. Quantitative data are available for only six main monoterpenes (*2*).

As occurs in all of the spiritous beverages, the presence of several volatile and semivolatile compounds strongly contributes to gin flavor perception. For this reason, extensive information about gin volatile composition is necessary for the characterization of distinct classes of products and as a basis for defining gin sensory quality.

The aim of the present study was to obtain wide information about the chemical composition of gin volatile fraction. For this purpose, a HS-SPME method coupled to GC-MS was developed and applied for the qualitative and semiquantitative characterization of the gin volatile fraction. Sampling, chromatographic conditions and method performances were evaluated. The developed method was applied for a comparative study of some of the most popular commercial London Dry Gins and gins with geographical indication (*6*). All of the samples were of distilled gin type, according to EEC Regulation 1576/89 (*1*).

MATERIALS AND METHODS

Reagents. Standard compounds 5-nonanol, myrcene, limonene, linalool, α-pinene, *β*-pinene, *p*-cymene, bornyl acetate, α-terpineol, *β*-citronellol, nerol, *t*-geraniol, valencene, farnesene, nonanal, and benzaldehyde were purchased from Sigma-Aldrich (St. Louis, MO). Caryophyllene oxide, elemol, and eudesmol were from M. C. M. Klosterfrau (Köln, Germany). Ethanol (96%) for analysis was from Panreac (Barcelona, Spain). The SPME fiber used was a divinylbenzene/Carboxen/poly(dimethylsiloxane) 50/30 *μ*m, 2 cm long (DVB/CAR/PDMS), from Supelco Ltd. (Bellefonte, PA).

Gin Samples. All of the samples were purchased from local retail outlets and pertained to the "distilled gin" type, according to EEC Regulation 1576/89 (*1*). Four groups of samples (G1−G4) were from the "London Dry Gin" type commercial brands, and two groups of samples (G5−G6) were from distinct geographical indications: Plymouth gin (U.K.) and Mahon gin (Spain). The London Dry Gin brands selected for the study were among the most consumed within their category (*6*).

Five stocks were analyzed for each London Dry Gin brand, and seven stocks were analyzed for each geographical denomination; all were analyzed in duplicate.

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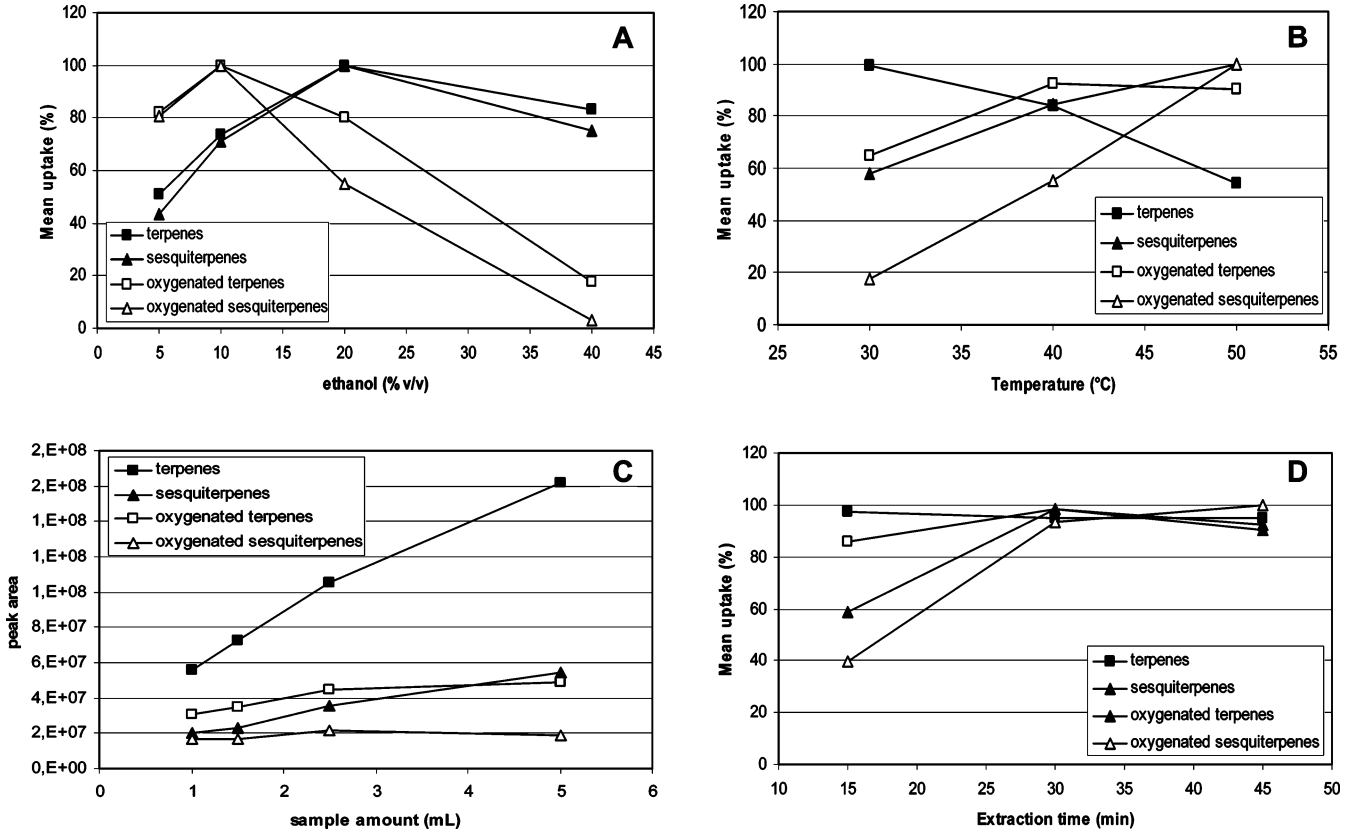

Figure 1. Mean percentage of uptake or peak areas of the main terpenic compound classes in gin as a function of distinct SPME extraction parameters: percentage of ethanol (**A**); sampling temperature (**B**); sample volume (**C**); extraction time (**D**).

SPME Sampling Conditions. Various parameters affecting the extraction efficiency were tested to find suitable SPME sampling conditions. To evaluate the effect of ethanol content on extraction efficiency, a gin sample was diluted with deionized water to obtain different ethanol concentrations (5, 10, 20, and 40% v/v).

To improve the extraction efficiency, various sampling temperatures (30, 40, and 50 °C) and sample volumes (1, 1.5, 2.5, and 5 mL) were tested. To determine the optimal extraction time, the fiber was held in the sample headspace for periods of 15, 30, and 45 min. All of the analyses were performed in duplicate. After comparison of the relative detector responses, the SPME sampling conditions were fixed as follows: 2.5 mL of a gin diluted at 10% ethanol (v/v) was placed into a 10 mL vial fitted with a silicone septum. The sample was placed in a silicon oil bath at 50 °C and maintained under magnetic stirring (700 rpm). After 5 min of sample conditioning, the fiber was exposed to the sample headspace for 30 min and then immediately desorbed in the gas chromatograph injector.

GC-MS Analysis. GC analyses were performed on an Agilent Technologies 6890N network gas chromatograph coupled to an Agilent Technologies 5973 network quadrupole mass selective spectrometer and provided with a split−splitless injection port. Helium was the carrier gas, at a linear velocity of 38 cm/s. Compounds were separated on Supelcowax-10 (Supelco Ltd., Bellefonte, PA) and on HP-5MS (Hewlett-Packard, Avondale, PA) capillary columns (both 30 m × 0.25 mm i.d., 0.25 μm film thickness). Column temperature was held at 40 °C for 5 min and increased to 220 °C at 3°C/min, holding for 10 min. The injector temperature was 260 °C, and the time of desorption of the fiber into the injection port was fixed at 2.5 min.

The temperatures of the ion source and the transfer line were 175 and 280 °C, respectively. Electron impact mass spectra were recorded at 70 eV ionization energy, 2 scan/s.

GC-MS analysis was carried out in the complete scanning mode (SCAN) in the 40−350 amu mass range.

Compounds were identified by comparison of their mass spectra and retention times with those of standard compounds or by comparison of the mass spectrum with those of the mass spectra library Wiley 6.

Table 1. Analytical Parameters Investigated for 13 Representative Compounds

	r^a	RF[b]	LOD[c] (μg L^{-1})	LOQ[d] (μg L^{-1})	RSD$_{\%}$[e] ($n = 5$)
α-pinene	0.999	1.8	0.004	0.013	4.4
β-pinene	0.999	1.9	0.004	0.012	4.4
β-myrcene	0.997	1.4	0.005	0.016	5.4
limonene	0.989	2.2	0.003	0.011	7.4
γ-terpinene	0.996	3.1	0.002	0.008	6.0
p-cymene	0.996	2.9	0.002	0.008	6.5
linalool	0.995	0.5	0.015	0.050	5.3
bornyl acetate	0.999	2.9	0.002	0.008	8.2
α-terpineol	0.984	0.4	0.019	0.064	3.8
valencene	0.991	10.8	0.001	0.002	11.7
β-citronellol	0.997	0.8	0.009	0.031	7.6
t-geraniol	0.997	0.3	0.020	0.066	7.2
caryophyllene oxide	0.974	2.2	0.003	0.010	13.5

[a] Correlation coefficient calculated with eight calibration points. [b] Response factor: ratio of relative area to concentration. [c] Limit of detection calculated as 3 times the baseline noise standard deviation referred to the sample, after correction of the dilution factor 1:4 employed. [d] Limit of quantification calculated as 10 times the baseline noise standard deviation referred to the sample, after correction of the dilution factor 1:4 employed. [e] Relative standard deviation (%) calculated at 2 mg L^{-1}.

Kovats indices and retention indices determined with reference to a homologous series of fatty acids methyl esters were calculated on two chromatographic capillary columns with distinct polarity and compared with retention indices available in the literature.

After chromatographic separation on a Supelcowax-10 capillary column, the quantitative determination was carried out by internal standard; samples were spiked with a solution of 5-nonanol to a final concentration of 1.5 mg L^{-1}.

Method Assessment. Calibration was performed by analyzing 90:10 water/ethanol solutions with different concentrations of various

Table 2. Components of Gin Headspace Identified by Reference Compounds or Tentatively Identified

no.	compound	ID[a]	RI[b]	KI Wax[c]	KI HP-5[d]	no.	compound	ID	RI	KI Wax	KI HP-5
1	α-pinene[e]	*f*	113	1017	929	**36**	*t*-geraniol[e]	*f*	520	1844	1245
2	α-thujene[e]	*g*	115	1022	923	**37**	α-cubebene[e]	*g*	321	1446	1340
3	camphene[e]	*g*	131	1056	942	**38**	α-copaene[e]	*g*	330	1470	1362
4	β-pinene[e]	*f*	148	1100	969	**39**	β-cubebene	*g*	362	1518	1377
5	sabinene[e]	*g*	155	1117	968	**40**	*t*-β-caryophyllene[e]	*g*	389	1571	1403
6	verbeneen	*g*	157	1119	948	**41**	β-elemene	*g*	390	1572	1403
7	δ-3-carene[e]	*g*	167	1141	1011	**42**	sesquiterpene ni[h]	–	407	1602	–
8	l-phellandrene[e]	*g*	175	1159	999	**43**	γ-elemene	*g*	413	1618	1421
9	β-myrcene[e]	*f*	177	1172	987	**44**	α-humulene[e]	*g*	422	1709	1435
10	α-terpinene[e]	*g*	181	1177	1011	**45**	*t*-β-farnesene[e]	*f*	431	1719	1446
11	DL-limonene[e]	*f*	190	1200	1025	**46**	γ-muurolene[e]	*g*	446	1723	1454
12	β-phellandrene[e]	*g*	194	1204	1026	**47**	sesquiterpene ni[h]	–	446	1726	–
13	γ-terpinene[e]	*f*	213	1244	1055	**48**	germacrene D	*g*	449	1733	1462
14	*t*-ocimene	*g*	213	1254	1046	**49**	α-selinene	*g*	453	1740	1470
15	*p*-cymene[e]	*f*	229	1275	1020	**50**	α-muurolene[e]	*g*	455	1748	1478
16	α-terpinolene	*g*	233	1283	1083	**51**	δ-cadinene[e]	*g*	471	1767	1504
17	*c*-rose oxide	*g*	250	1369	1107	**52**	γ-cadinene[e]	*g*	474	1768	1504
18	verbenyl ethyl ether	*g*	251	1371	–	**53**	cadina-1,4-diene	*g*	482	1778	1515
19	citronellal	*g*	340	1477	1050	**54**	sesquiterpene ni[h]	–	488	1784	1509
20	campholenal	*g*	344	1482	1086	**55**	germacrene B	*g*	503	1800	1535
21	camphor[e]	*g*	354	1495	1137	**56**	sesquiterpene ni[h]	–	529	1856	1629
22	linalool[e]	*f*	377	1552	1097	**57**	α-calacorene	*g*	535	1893	1519
23	*c*-sabinene hydrate	*g*	381	1556	1060	**58**	sesquiterpene ni[h]	–	563	1927	1669
24	bornyl acetate[e]	*f*	386	1565	1282	**59**	caryophyllene oxide	*f*	579	1953	1558
25	l-4-terpineol[e]	*g*	400	1593	1175	**60**	torreyol	*g*	618	2041	1604
26	myrtenal	*g*	409	1602	1190	**61**	elemol	*f*	630	2066	–
27	α-terpineol[e]	*f*	447	1736	1186	**62**	spathulenol	*g*	650	2104	1571
28	terpenyl acetate[e]	*g*	444	1731	1342	**63**	*t*-cadinol	*g*	673	2153	1636
29	neryl acetate	*g*	461	1754	–	**64**	*t*-muurulol	*g*	680	2168	1649
30	geranyl acetate[e]	*g*	476	1772	1381	**65**	eudesmol	*f*	695	2203	1655
31	cuminal	*g*	485	1776	1234	**66**	α-cadinol	*g*	700	2210	1651
32	β-citronellol[e]	*f*	481	1780	1227	**67**	ni[h] (*m*/*z* 139, 167)	–	243	1304	1150
33	myrtenol	*g*	492	1788	1192	**68**	nonanal	*f*	256	1398	1101
34	nerol[e]	*f*	497	1797	1202	**69**	benzaldehyde	*f*	362	1516	959
35	*t*-carveol	*g*	513	1825	1240	**70**	2-undecanone	*g*	397	1588	1282

[a] Identification method. [b] Retention indices based on fatty acid methyl esters (Supelcowax-10). [c] Kovats indices on Supelcowax-10. [d] Kovats indices on HP-5. [e] Previously detected in gin (*2*). [f] Identified by comparison with standard compounds. [g] Tentatively identified by mass spectra and retention indices. [h] Not identified.

representative standard compounds including oxygenated and nonoxygenated mono- and sesquiterpenes. Standard solutions were prepared in the range of 0.01−8 mg L^{-1} (0.01, 0.1, 1, 2, 4, 6, and 8 mg L^{-1}) and analyzed in duplicate under the same conditions described for samples.

The method was assessed by determining relative response factors (with respect to the internal standard 5-nonanol), linearity of response (*r* values), repeatability, and limits of detection (LOD) and quantification (LOQ). Repeatability of the method was tested by repeating the analysis of a 2 mg L^{-1} standard mixture five times. LODs and LOQs were calculated as $LOD = 3\delta/m$ and $LOQ = 10\delta/m$, respectively, according to the method of Long et al. (*7*) and IUPAC (*8*) definitions, where δ is the standard deviation of the baseline noise and *m* is the slope of the calibration curve.

RESULTS AND DISCUSSION

SPME Conditions. The development of a suitable SPME method for the analysis of gin volatiles involved the selection and evaluation of a number of parameters that influence the SPME extraction. These included the temperature and time of extraction, the sample volume, and the percentage of ethanol in the sample. Among the commercially available fibers, the Carboxen-based coatings showed the better efficiency for a wide number of volatile organic compounds (*9*, *10*). In this study, the three-phase coating PDMS/Car/DVB was chosen for its affinity with compounds of both low and medium molecular weight (*11*).

In SPME analysis of spirits and distillates, ethanol concentration is among the main factors affecting the extraction efficiency and causing chromatographic interferences. On the one hand, high concentrations of ethanol in the aqueous matrix favor the solubilization of the organic compounds, decreasing their volatility. On the other hand, large amounts of ethanol in the sample headspace compete with the analytes of interest for the adsorption sites on the SPME coating (*12*, *13*).

In the present work, two factors were evaluated to minimize the effect of ethanol and its adsorption on the fiber coating: the decrease of ethanol concentration by sample dilution and the modification of its distribution constant by increasing the extraction temperature.

Figure 1A shows the percentage uptake of the main classes of compounds identified in the gin volatile fraction, as a function of the percentage of ethanol in the sample (v/v). By diluting the sample from 40 to 20% ethanol (v/v), the uptake of all the compounds increased, showing an improvement in the extraction efficiency due to decrease of ethanol. Further dilution to 10% ethanol (v/v) simultaneously caused the increase of the oxygenated terpenes response plus a decrease of nonoxygenated terpenes. Possible explanations for these results may be a higher competition effect of ethanol with oxygenated terpenes or a stronger effect on their solubilization. When the concentration of 5% of ethanol was reached, the uptake of all the analyzed compounds decreased due to the dilution effect. The ethanol concentration was then fixed at 10% (v/v). This concentration allowed the maximum uptake of oxygenated terpenes and sesquiterpenes, the responses of which in gin were generally lower than those of nonoxygenated species (**Figure 1C**).

Figure 1B represents the mass of volatiles adsorbed by the fiber, expressed as percentages, as a function of the extraction temperature. As expected, the uptake of less volatile compounds increased at higher temperatures because of the improvement of the mass-transfer process from the sample to the headspace. This was the case in sesquiterpenes and in particular oxygenated

Table 3. Content of Volatile Compounds in Four London Dry Gins and Two Gins with Geographical Indication

			mean concentration (mg L^{-1})					
			London Dry Gins ($n = 10$)				geographical indications ($n = 14$)	
no.	compound	RF[a]	1	2	3	4	5	6
1	α-pinene	*b*	2.25	1.95	3.60	2.42	6.12	5.65
2	α-thujene	*b*	0.24	0.23	0.27	0.20	0.29	0.70
3	camphene	*b*	0.06	0.07	0.09	0.07	0.16	0.10
4	β-pinene	*c*	0.66	0.57	0.39	0.37	1.53	1.35
5	sabinene	*c*	0.66	1.10	1.02	0.96	0.09	2.53
6	verbenene	*c*	0.05	0.06	0.05	0.06	0.06	0.32
7	δ-3-carene	*c*	0.11	0.03	0.06	0.03	0.09	0.05
8	l-phellandrene	*c*	0.09	0.08	0.06	0.06	0.08	0.19
9	β-myrcene	*d*	2.38	3.95	4.66	5.01	6.17	11.09
10	α-terpinene	*e*	0.39	0.31	0.32	0.31	0.61	0.65
11	DL-limonene	*e*	4.84	8.57	1.22	1.33	17.21	5.74
12	β-phellandrene	*e*	0.29	0.54	0.20	0.22	0.46	0.64
13	γ-terpinene	*f*	1.32	1.37	1.16	1.17	2.87	1.51
14	*t*-ocimene	*f*	0.06	0.06	0.05	0.11	0.06	0.04
15	*p*-cymene	*g*	1.13	0.60	0.53	0.73	0.85	1.74
16	α-terpinolene	*f*	0.25	0.27	0.28	0.31	0.49	0.59
	sum of monoterpenes		14.77	19.75	13.95	13.35	37.14	32.89
17	*c*-rose oxide		nq°	nq	nq	nq	nq	nq
18	verbenyl ethyl ether	*h*	2.55	3.79	2.64	4.81	3.27	24.43
19	citronellal	*h*	0.08	0.14	0.09	0.17	0.06	0.41
20	campholenal	*h*	0.51	0.64	0.52	0.79	0.55	4.55
21	camphor	*h*	0.83	1.13	1.19	1.54	1.19	0.85
22	linalool	*h*	10.96	18.36	23.18	36.99	16.83	1.93
23	*c*-sabinene hydrate		nq	nq	nq	nq	nq	nq
24	bornyl acetate	*i*	0.18	0.26	0.20	0.35	0.35	2.01
25	l-4-terpineol	*j*	0.32	0.25	0.22	0.29	0.40	0.79
26	myrtenal		nq	nq	nq	nq	nq	nq
27	α-terpineol	*i*	1.13	1.60	1.42	1.89	3.80	9.03
28	terpenyl acetate	*j*	0.08	0.12	0.10	0.15	0.32	0.71
29	neryl acetate	*i*	0.15	0.17	0.05	0.10	0.18	0.31
30	geranyl acetate	*i*	0.70	1.11	1.62	2.09	1.53	0.25
31	cuminal	*k*	0.10	0.10	0.08	0.11	0.07	0.96
32	β-citronellol	*k*	0.05	0.08	0.11	0.22	0.10	1.97
33	myrtenol	*k*	0.02	0.02	0.02	0.04	0.02	0.37
34	nerol	*l*	0.01	0.01	0.01	0.02	0.01	0.10
35	*t*-carveol	*l*	0.06	0.08	0.05	0.10	0.06	0.54
36	*t*-geraniol	*l*	0.19	0.33	0.32	0.54	0.21	0.63
	sum of oxygenated monoterpenes		16.69	26.48	30.31	48.05	25.10	38.45
37	α-cubebene	*m*	0.09	0.07	0.10	0.12	0.12	0.24
38	α-copaene	*m*	0.10	0.04	0.07	0.07	0.10	0.05
39	β-cubebene	*m*	0.04	0.04	0.04	0.06	0.05	0.14
40–41	*t*-β-caryophyllene and β-elemene	*m*	0.41	0.47	0.60	0.66	0.77	0.93
42	sesquiterpene ni	*m*	0.02	0.02	0.02	0.02	0.02	0.08
43	γ-elemene	*m*	0.22	0.39	0.37	0.42	0.65	0.92
44	α-humulene	*m*	0.25	0.28	0.35	0.42	0.47	0.90
45	*t*-β-farnesene	*m*	0.02	0.04	0.06	0.05	0.09	0.05
46	γ-muurolene	*m*	0.07	0.09	0.11	0.12	0.19	0.16
47	sesquiterpene ni	*m*	0.02	0.02	0.03	0.05	0.07	0.12
48	germacrene D	*m*	0.13	0.29	0.38	0.42	0.57	0.62
49	α-selinene	*m*	0.06	0.07	0.09	0.09	0.15	0.13
50	α-muurolene	*m*	0.08	0.08	0.10	0.12	0.14	0.15
51–52	δ- and γ-cadinene	*m*	0.32	0.52	0.68	0.76	1.15	0.93
53	cadina-1,4-diene	*m*	0.02	0.03	0.04	0.04	0.04	0.11
54	sesquiterpene ni	*m*	0.02	0.03	0.04	0.04	0.05	0.05
55	germacrene B	*m*	0.08	0.12	0.12	0.15	0.18	0.10
56	sesquiterpene ni	*m*	0.01	0.03	0.03	0.06	0.11	0.20
57	α-calacorene	*m*	0.02	0.02	0.02	0.04	0.03	0.19
58	sesquiterpene ni	*m*	0.03	0.07	0.08	0.13	0.25	0.63
	sum of sesquiterpenes		2.32	3.23	4.02	4.60	6.34	7.63
59	caryophyllene oxide	*n*	0.18	0.15	0.21	0.39	0.09	5.13
60	torreyol	*n*	0.08	0.09	0.13	0.19	0.14	1.52
61	elemol	*n*	0.01	0.02	0.01	0.02	0.01	0.32
62	spathulenol	*n*	0.05	0.05	0.06	0.08	0.04	1.29
63	*t*-cadinol	*n*	0.03	0.04	0.05	0.07	0.08	0.97
64	*t*-muurulol	*n*	0.03	0.04	0.06	0.08	0.12	1.27
65	eudesmol	*n*	0.01	0.02	0.01	0.02	0.01	0.18
66	α-cadinol	*n*	0.06	0.08	0.09	0.12	0.18	1.45
	sum of oxygenated sesquiterpenes		0.46	0.50	0.61	0.97	0.67	12.13

[a] Relative response factor employed for quantification. [b] RF of α-pinene. [c] RF of β-pinene. [d] RF of β-myrcene. [e] RF of limonene. [f] RF of γ-terpinene. [g] RF of *p*-cymene. [h] RF of linalool. [i] RF of bornyl acetate. [j] RF of α-terpineol. [k] RF of β-citronellol. [l] RF of *t*-geraniol. [m] RF of valencene. [n] RF of caryophyllene oxide. [o] nq, not quantified, unresolved peaks.

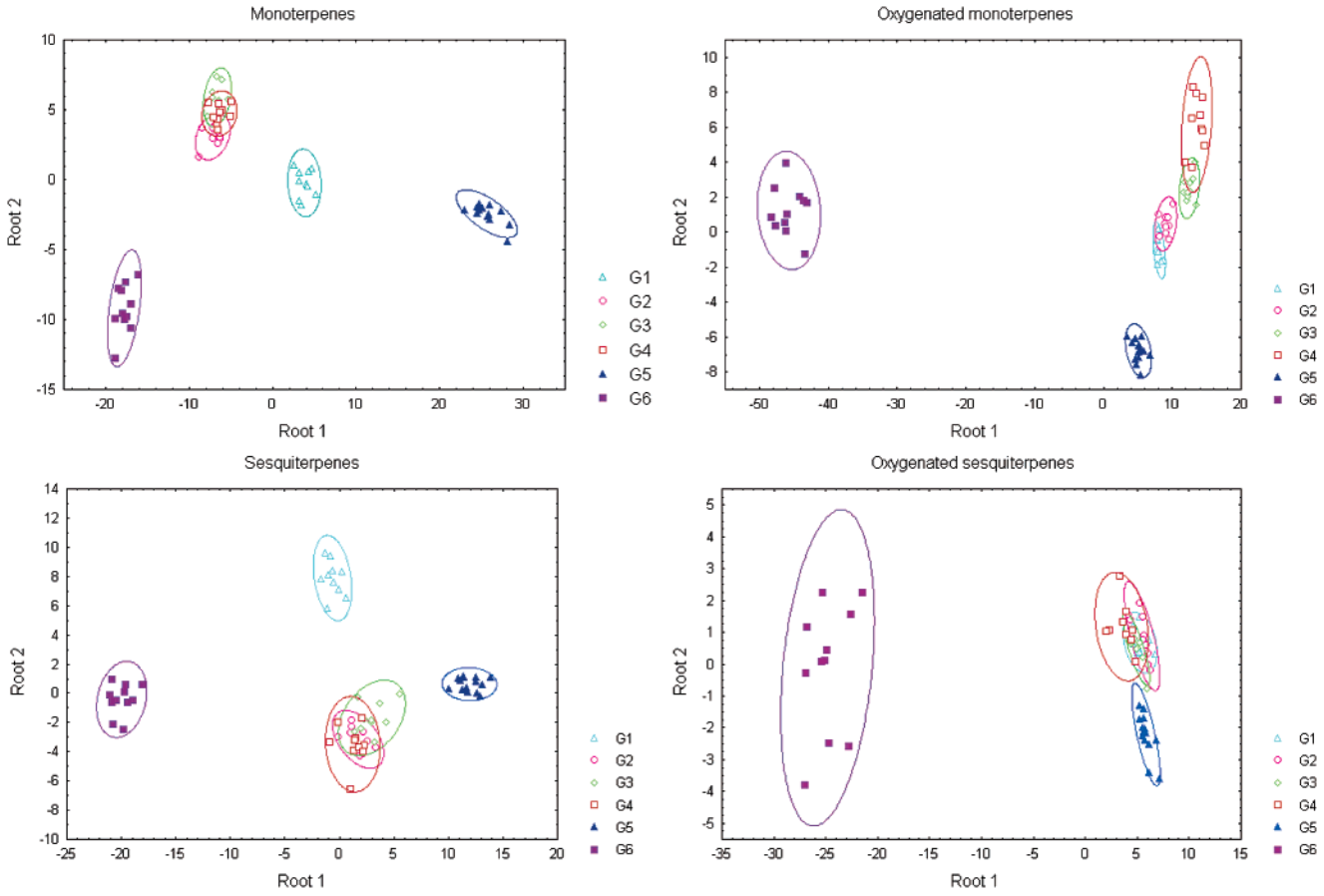

Figure 2. Discriminant analysis of gin samples as a function of their oxygenated and nonoxygenated mono- and sesquiterpenes composition.

sesquiterpenes. On the contrary, the uptake of oxygenated terpenes did not increase over 40 °C, and nonoxygenated terpenes responses decreased at temperatures above 30 °C. The extraction temperature was fixed at 50 °C to improve sensitivity for the less volatile compounds and to minimize the adsorption of ethanol. Although the high temperature improves the mass transfer of analytes from the sample to the headspace, it negatively affects the exothermic process of adsorption of analytes, especially for very volatile compounds such as monoterpenes and ethanol (*14*).

Several volumes of sample were tested (**Figure 1C**). A correlation between the amount of analyte adsorbed by the fiber and the sample volume was found when there is a high affinity with the fiber coating (*15*). Nonoxygenated species showed a higher correlation with the sample volume, suggesting a better affinity of these compounds with the fiber. The sample volume was fixed at 2.5 mL to avoid saturation of the fiber by the most volatile species.

Finally, by testing different extraction times, it was observed that the equilibrium was reached after 30 min of sampling (**Figure 1D**).

Method Assessment. After the determination of suitable SPME parameters, the method was assessed by determining relative response factors, linearity of response, repeatability, and limits of detection and quantification for a number of representative compounds present in gin headspace (**Table 1**). A satisfactory linearity was obtained within the whole interval of concentration tested, and the relative standard deviation (RSD) calculated at a concentration of 2 mg L^{-1} was <10% for most of the compounds. Only valencene and caryophyllene oxide showed slightly higher RSDs. The lowest response factors were observed for oxygenated monoterpenes, particularly for alcoholic derivatives, whereas the highest value was calculated for valencene. LODs and LOQs were in the ranges of 0.001−0.02 and 0.002−0.066 μg L^{-1}, respectively.

Characterization of Gin Volatile Fraction. The analysis of gins pertaining to six different commercial brands, including two geographic denominations ($n = 10$ for each London Dry Gin and $n = 14$ for each geographic denomination), identified 70 compounds. The identification results are described in **Table 2**, together with the identification methods employed. The detected compounds were mainly mono- and sesquiterpenic hydrocarbons and their oxygenated derivatives. These had only been partially detected previously in gin samples.

The mean concentrations of volatile compounds found in each group of samples are presented in **Table 3**, expressed in milligrams per liter. The same table shows the relative response factors used for quantification. The concentrations of all the detected compounds, except β-cubebene, resulted in significant differences among the gin brands analyzed ($p < 0.05$, data not shown).

The main monoterpenes detected in gin samples were α-pinene, β-myrcene, and limonene, followed by γ-terpinene, *p*-cymene, sabinene, and β-pinene (**Table 3**), reflecting the monoterpenic composition of juniper berry extract (*16*−*18*). Some of these monoterpenes are also abundant in other aromatic plants employed in gin production. In fact, in the essential oil of citric fruits, limonene and γ-terpinene may represent 65−95 and 10%, respectively (*19*−*21*).

The highest contents of juniper characteristic monoterpenes were found in samples with geographic denomination G6, whereas samples with geographic denomination G5 showed the

highest concentrations of limonene and γ-terpinene. This is probably due to the use of citric species during gin aromatization.

Oxygenated monoterpenes were represented by monoterpenic alcohols, esters, ketones, and aldehydes. In all of the samples, except G6, linalool was the most abundant among these compounds. Linalool is present in traces in juniper berries (*17*), whereas it is the major compound in the essential oil of coriander, in which it may represent >60% (*22*, *23*). Coriander seeds are well-known ingredients in gin aromatization (*2*), and linalool concentration may indicate the proportion of coriander employed for this operation. Coriander seems to be a common ingredient of the gins analyzed in this study, except in the geographic denomination G6, in which the linalool mean concentration was very low. The highest concentration of this compound was present in the London Dry Gin samples of the G4 group.

α-Terpineol and other compounds tentatively identified as verbenyl ethyl ether and geranyl acetate were among the major oxygenated monoterpenes. α-Terpineol is known to be one of the main volatile components of juniper berries, whereas geranyl acetate was not detected in juniper berries or leaves (*16*−*18*), nor in other botanical species used in gin production. Nevertheless, it had been previously identified in gin samples (*2*). Verbenyl ethyl ether was not detected in juniper or other botanical species, nor in gin samples.

With the exception of linalool and geranyl acetate, the samples G6 showed the highest contents of oxygenated monoterpenes. These samples contained the highest levels of some major oxygenated monoterpenes found in juniper berries, such as α-terpineol, I-4-terpineol, and bornyl acetate (*5*, *16*−*18*).

The highest concentrations of sesquiterpenic hydrocarbons found in the gin samples were given by the sum of γ- and δ-cadinene and the sum of caryophyllene and β-elemene, followed by γ-elemene, α-humulene, and germacrene D. This sesquiterpenic composition is comparable with the composition reported for juniper berries (*16*). The gins with geographic denomination showed the highest amounts of the main sesquiterpenes, whereas the lowest levels were observed in the London Dry Gins G1 and G2. In particular, the G6 samples contained the highest amounts of caryophyllene, β-elemene, γ-elemene, and α-humulene, whereas G5 samples showed the highest amounts of cadinene isomers.

The oxygenated sesquiterpenes identified in gins were all alcoholic derivatives of sesquiterpene hydrocarbons. Some of them have been described as components of the juniper berry and leaf volatile fractions (*16*−*18*), but they had not been reported in gin samples.

The analysis of volatile compounds could prove to be useful in the classification and authentication of distilled gins for defining a geographic denomination. The discriminant analysis was performed to classify the samples into groups according to the chemical composition of their volatile fraction. To assess the significance of the discriminant analysis, the Mahalanobis distance square and the *p* levels were calculated (data not shown) and revealed that all brands possess significantly different terpenic composition. This does not apply to oxygenated sesquiterpenes, which significantly differentiate the samples with geographic denomination. **Figure 2** displays the plots of the discriminant analysis based on the composition in nonoxygenated and oxygenated mono- and sesquiterpenes. The gins with geographical indication were clearly distinguished by their oxygenated and nonoxygenated terpenic composition. It is worth noting that samples of G6 showed the highest differentiation based on the oxygenated terpenes. In addition to distinguishing the gins with geographical indication, mono- and sesquiterpenic hydrocarbons allowed one of the London Dry Gins analyzed, G1, to be clearly distinguished

In conclusion, the application of SPME to the analysis of gin headspace enabled the identification and quantification of an extensive number of volatile and semivolatile compounds, which could contribute to the organoleptic characteristics of the gins. The results obtained may be useful for further studies on the sensory properties of gin. The terpenic composition of gin may also be used to distinguish samples from different commercial brands and gins with geographical indication and to indicate the type of botanical ingredients employed for gin aromatization and their proportions.

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