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Characterization of rum using solid-phase microextraction with gas chromatography–mass spectrometry

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Abstract

Headspace solid-phase microextraction was used to extract and analyze volatile compounds in different aged rums. The interference of ethanol was resolved with a dilution of the sample at 12% v/v. The extraction procedure, using a 100 μm PDMS fibre with 35 min at 30 °C, permitted the isolation of a large quantity of volatile compounds. One hundred and eighty-four volatile compounds were identified, including 64 esters, 47 benzenic compounds, 16 terpenoids, 14 alcohols, 10 acetals, 9 aldehydes, 6 phenols, 6 ketones, 6 furans, 3 acids and 3 benzopyrans.

Semi-quantitative analysis, based on area percent, showed very good reproducibility. The use of only 15 volatile compounds permits a differentiation between the 3- and 7 year-old rums.

Keywords: Rum; Volatile compounds; SPME; GC–MS

1. Introduction

Rum is a cane spirit obtained by distillation of sugar cane molasses, after fermentation with yeast, and subsequent aging in oak barrels, where the spirit acquires its special characteristics of flavour and aroma during the time it is in contact with the wood. This stage, also termed maturation, where the spirit extracts a series of compounds from the wood that have a positive influence on the sensory characteristics of the final product, together with the fermentation and distillation, are the most important stages in the presence of different volatile compounds (Nykänen & Nykänen, 1983; Pino, 1996).

These compounds comprise mainly fusel alcohols, ethyl acetate and acetic acid, which are present in relatively large amounts (Nykänen & Nykänen, 1983; Pino, 1996). These compounds may be determined by direct gas chromatography as pre-treatment is not essential. However, esters, carbonyl compounds and other minor volatile congeners are present at much lower concentrations and, therefore, their determination often requires the use of a pre-concentration step.

Liquid–liquid extraction, static and dynamic headspace analyses have been commonly used for the analysis of volatile flavour compounds in foods and beverages. Their advantages and disadvantages have been reviewed (Acree & Teranishi, 1993; Maarse & Ven der Heij, 1994). Liquid–liquid extraction, often applied to distilled spirits (Herranz, de la Serna, Barro, & Martín-Alvarez, 1990; Pino, Villarreal, & Roncal, 1994; Pino, Pérez, & Nuñez de Villavicencio, 1996; Pino & Rosado, 1999; Schreier, Drawert, & Winkler, 1979), is not efficient in extracting trace constituents and this procedure is labour-intensive and suffers from the formation of artifacts and low recoveries. There are virtually no reports on the study of volatile flavour compounds in distilled beverages by headspace methods.

Solid-phase microextraction (SPME) is a solvent-free extraction technique that allows the extraction and the con-

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centration steps to be performed simultaneously (Pawliszyn, 1997). Its main advantages are simplicity and little sample manipulation. The SPME uses a fused silica microfibre coated with a stationary phase, which is immersed directly into the liquid sample or into the headspace above it. Recently, direct sampling (Ng, 1999) and headspace sampling (Pino et al., 2002) have been demonstrated to be very efficient for extracting volatile flavour compounds in rum. It is known that, in general, the extraction times for volatile compounds are shorter for headspace SPME than for direct extraction, and that the lifetime of the fibre is extended using the headspace procedure (Pawliszyn, 1997).

In the present study, we used headspace SPME-GC–MS to analyze the volatile compounds from different aged rums.

2. Materials and methods

2.1. Materials

Six samples (40% alcohol) of four commercially available Cuban brands of rum, manufactured by traditional aging techniques, were grouped according to the aging time stated on the label. The commercial brands analyzed comprised three samples of 3 year-old (coded as 3B, 3C and 3D) and three other samples of 7 year-aged rums (coded as 7E, 7F and 7G). Also, a white cane spirit (''aguardiente''), the raw material used to manufacture the rum, was obtained from the main commercial Cuban distillery. Authentic compound standards were from various suppliers and were used without further purification.

2.2. Solid-phase microextraction

The SPME holder, for manual sampling, and polydimethylsiloxane fibres (PDMS 100 μm) used in this study, were purchased from Supelco (Bellefonte, USA). The fibres were conditioned by inserting them into the GC system injector at 250 °C for 1 h and they were immediately used to prevent contamination.

In order to obtain the best results, the experimental conditions were selected according to the results reported earlier for the analysis of higher fatty acid ethyl esters (Pino et al., 2002). In the optimized procedure, 10 ml of sample (previously diluted to 12% ethanol) were placed in a 20 ml vial with 1.8 g of NaCl. Then the vial was hermetically sealed with silicone septa and shaken to obtain a homogeneous mixture. The headspace SPME of the sample was done at 30 °C for 35 min with constant magnetic stirring (500 rpm). When the extraction step was finished, the SPME fibre was removed from the vial and inserted into the injection port of the GC for thermal desorption of the analytes at 250 °C for 1 min in splitless mode. All analyses were done in triplicate. Blank analyses were also done.

2.3. Identification of the volatile compounds

The analyses were carried out on a Hewlett–Packard 6890 gas chromatograph equipped with a flame ionization detector (FID). The injection was done in splitless mode for 1 min using an inlet of 0.75 mm I.D. which improved the GC resolution. The temperature of both the injector and detector was 250 °C. The separations were performed using a SPB-5 column (30 m × 0.25 mm × 0.25 μm) (Supelco, Inc., Bellefonte, USA) with an oven temperature programme of 60 °C (2 min), 4 °C/min to 250 °C (20 min). The carrier gas was helium with a flow-rate of 1 ml/min.

To identify the volatile compounds, which were also extracted by the fibre, a Hewlett–Packard series 6890 (series II) gas chromatograph equipped with a HP-5973 mass-selective detector was used. The chromatographic conditions were the same as those described for GC–FID. The detector operated in impact electron mode (70 eV) at 230 °C. Detection was performed in the scan mode between 30 and 400 amu. Compounds were identified by comparing their spectra to those of the Wiley and NIST libraries or our FLAVORLIB library and also by comparison of their GC retention indices to those of standard compounds and data from the literature (Adams, 2001).

2.4. Quantitative measurements

The total content of the compound of each analysis was defined by integrating the peak areas of the volatile compounds. Mean peak area percentages and standard deviations from replicate analyses were calculated from the total content of volatiles on the chromatograms.

2.5. Statistical analysis

Mean peak area and standard deviations from replicate analyses were calculated and were comparing using the *F*-Fisher test. The Statistica 6.0 package (StatSoft Inc., 1998) was used for principal component analysis from correlation matrix in order to examine the relationships among the variables and to discover natural groupings of the samples. The variables were previously standardized ([raw score − mean]/standard deviation).

3. Results and discussion

The high ethanol concentration of the rums required dilution before the extraction procedure. Ethanol is one of the major rum constituents that can compete with the other volatiles in the extraction by the fibre. In fact, some authors (Ebeler, Terrien, & Butzke, 2000; Mestres, Sala, Martí, Busto, & Guasch, 1999; Ng, 1999) have found that an increase in the ethanol content decreases the extraction efficiency. To check this effect, a sample of rum with 40% v/v of ethanol was diluted to obtain different solutions with alcohol contents of 5%, 12% and 20% v/v and these were analyzed. The total area of chromatograms (without the

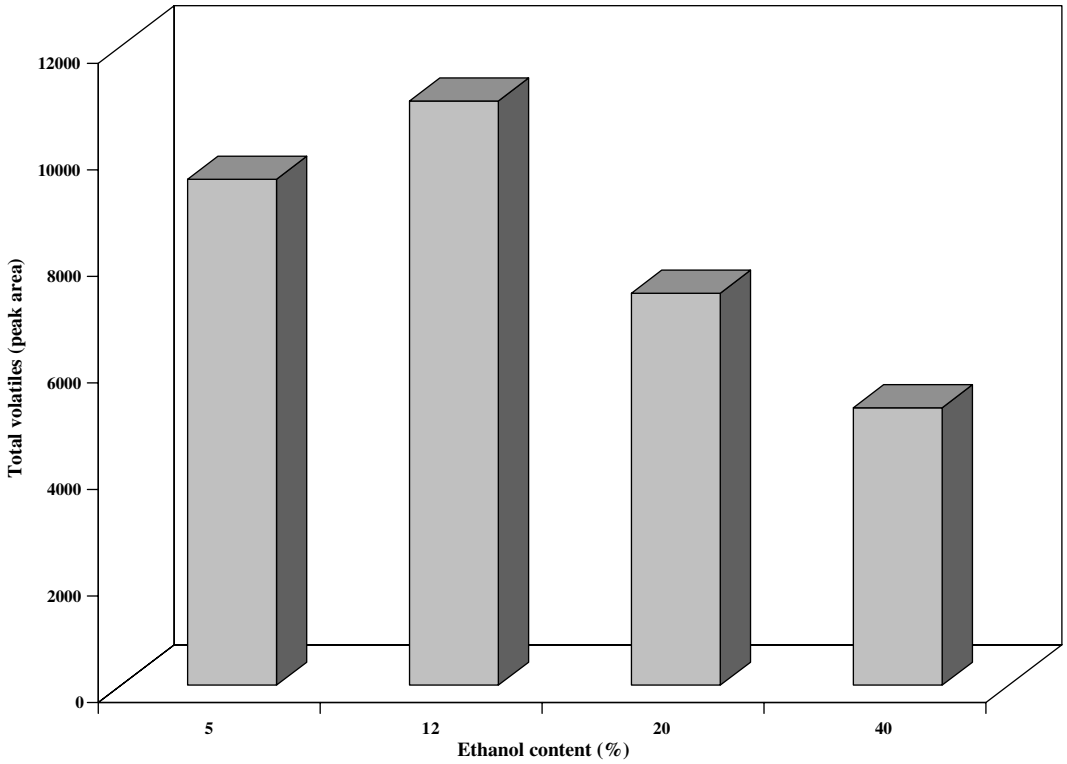

Fig. 1. Effect of initial ethanol content on total volatiles.

ethanol peak) obtained at different ethanol contents was calculated (Fig. 1).

Despite the fact that the PDMS fibre coating was the most non-polar commercially available, it still had sufficient affinity for ethanol such that the resolution of subsequent peaks in the chromatograms was adversely affected by the tail of the ethanol peak if the samples were not diluted. The data obtained show that the higher the ethanol concentration, the lower was the extraction efficiency. However, with 5% of ethanol, there was also a great dilution of the minor volatile components; therefore 12% of ethanol was fixed for subsequent analysis. No significant differences were found in the qualitative profiles. With these conditions, the determination of the relative concentration was generally reproducible within 2–10% RSD.

A typical SPME-GC profile of 7 year-old rum is shown in Fig. 2. The compounds identified are listed in Table 1, together with their relative concentrations in the extract (based on GC–MS peak area percentage).

Chemical functionalities confirmed to be present among the volatile compounds of rum include terpenoids, alcohols, acetals, aldehydes, phenols, ketones, furans, acids and benzopyrans. One hundred and eighty-four volatile compounds were identified in rum, and sixty-eight of these have not been previously identified in light rum (Pino, 1996; Pino et al., 1996), although some of them have been reported in dark rum (Nijssen, Visscher, Maarse, Willemsens, & Boelens, 1996). However, the aroma of rum is not necessarily connected with the number of peaks in the chromatogram. The concentration in the sample and its odour threshold are much more important, and should be studied by other techniques, such as olfactometric detection (GCO).

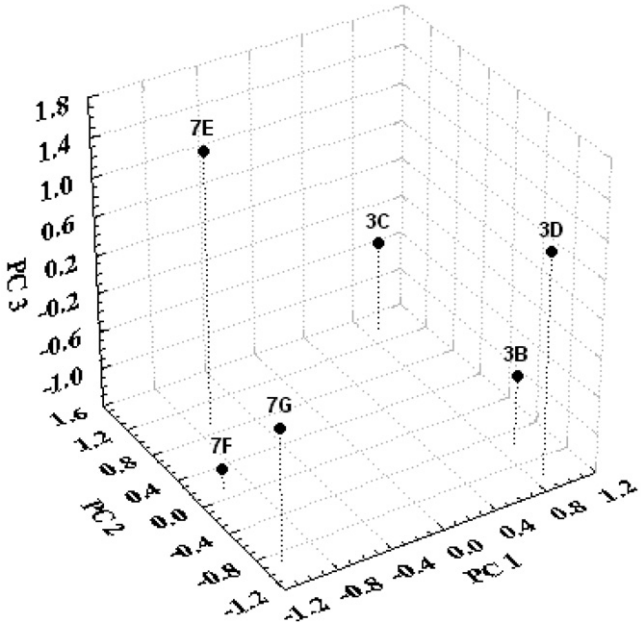

Fig. 2. Graphical projection of the rum samples onto PCA component axes.

In terms of the numbers of components identified, esters represent the largest group, with 64 individual compounds detected in the rum extracts. Of these, many were ethyl

Table 1
Volatile compounds identified in rum (% in total extract)

Compound	RI[a]	ID[b]	A	3B	3C	3D	7E	7F	7G
Acetaldehyde	435	MS, RI	<0.1	0.1	0.1	0.1	<0.1	0.1	<0.1
Ethanol	439	MS, RI	11.8a	11.9a	12.1a	12.1a	11.8a	12.1a	12.0a
1-Propanol	568	MS, RI	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethyl acetate	577	MS, RI	0.3a	1.1b	1.0b	1.0b	3.4c	3.6c	4.4c
Acetic acid	600	MS, RI	<0.1	–	–	–	<0.1	<0.1	<0.1
Isobutanol	622	MS, RI	0.5	<0.1	0.1	0.1	<0.1	<0.1	<0.1
3-Methylbutanal	650	MS, RI	<0.1	<0.1	<0.1	–	<0.1	<0.1	<0.1
Diethoxymethane	679	MS	–	–	–	–	<0.1	<0.1	<0.1
2-Pentanone	689	MS, RI	<0.1	<0.1	–	<0.1	<0.1	<0.1	<0.1
Ethyl propanoate	717	MS, RI	–	–	–	–	–	–	<0.1
Propyl acetate	719	MS, RI	<0.1	–	–	–	–	–	–
Acetal	730	MS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3-Methyl-1-butanol + 2-Methyl-1-butanol	736	MS, RI	5.2a	5.4a	5.4a	5.6a	5.4a	5.7a	4.2b
Ethyl isobutanoate	756	MS, RI	0.1a	0.9b	0.8b	0.9b	0.9b	0.9b	0.9b
Toluene	773	MS, RI	<0.1	<0.1	–	<0.1	–	<0.1	<0.1
Isobutyl acetate	777	MS, RI	<0.1	–	<0.1	<0.1	<0.1	<0.1	0.1
Propanoic acid	789	MS, RI	<0.1	–	<0.1	–	–	<0.1	–
Ethyl butanoate	804	MS, RI	0.1a	0.2a	0.2a	0.2a	0.2a	0.3a	0.3a
4,5-Dihydro-2-methyl-3(2H)-furanone[c]	814	MS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	–
3-Methylphenol	825	MS, RI	<0.1	–	–	–	–	–	–
2-Furfural	830	MS, RI	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethyl 2-methylbutanoate	849	MS, RI	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	–
Ethyl isopentanoate	856	MS, RI	<0.1	0.1	0.2	0.1	0.2	0.2	0.1
(*Z*)-3-Hexenol	859	MS, RI	<0.1	–	–	–	–	–	–
1,1-Diethoxy-2-methylpropane	861	MS	0.1	0.1	<0.1	0.1	<0.1	<0.1	0.1
Ethylbenzene	864	MS	0.1	<0.1	–	–	–	–	–
1-Hexanol	867	MS, RI	-	<0.1	–	<0.1	<0.1	–	–
m-Xylene	870	MS, RI	0.2	<0.1	0.1	0.1	<0.1	<0.1	0.1
3-Methyl-1-butyl acetate	876	MS, RI	0.2a	0.1a	0.4b	0.4b	0.3b	0.4b	0.4b
2-Methyl-1-butyl acetate	880	MS, RI	0.1	0.1	0.2	0.2	0.2	0.1	–
2-Heptanone	889	MS, RI	<0.1	–	–	<0.1	<0.1	–	–
Styrene	895	MS	<0.1	0.1	–	0.1	<0.1	0.1	0.6
o-Xylene	897	MS, RI	0.1	–	–	–	–	–	–
Ethyl pentanoate	898	MS, RI	0.1a	0.2a	0.4b	0.2a	0.2a	0.2a	0.1a
Butyl isobutanoate	910	MS, RI	–	–	<0.1	–	<0.1	<0.1	–
Ethyl sorbate[c]	918	MS	<0.1	–	–	–	<0.1	–	–
α-Pinene	939	MS, RI	–	–	<0.1	<0.1	–	<0.1	<0.1
1,1-Diethoxy-3-methoxybutane[c]	956	MS	0.2	<0.1	0.2	0.1	0.1	<0.1	0.2
1-Ethyl-3-methylbenzene[c]	959	MS	<0.1	–	–	–	–	–	0.2
Benzaldehyde	961	MS, RI	–	0.1a	0.1a	0.1a	0.4b	0.8b	0.5b
Ethyl isohexanoate[c]	969	MS, RI	<0.1	0.1	<0.1	<0.1	–	<0.1	<0.1
1,3,5-Trimethylbenzene[c]	970	MS	<0.1	–	–	–	–	–	<0.1
1-(1-ethoxyethoxy)-Pentane[c]	973	MS	0.1	<0.1	0.1	–	–	<0.1	<0.1
1-Octen-3-ol	978	MS, RI	<0.1	<0.1	0.1	0.1	–	<0.1	<0.1
Myrcene	991	MS, RI	–	–	–	<0.1	<0.1	–	–
Butyl butanoate[c]	993	MS, RI	<0.1	–	–	–	–	–	–
Ethyl hexanoate	996	MS, RI	1.0a	0.8a	1.2a	1.8a	1.0a	1.2a	0.6a
3-Methyl-1-butyl isobutanoate	1005	MS, RI	0.1	–	0.1	–	0.1	<0.1	–
Hexyl acetate	1008	MS, RI	<0.1	–	–	0.1	–	–	–
p-Cymene[c]	1026	MS, RI	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Limonene	1031	MS, RI	0.1	<0.1	0.1	0.1	0.3	0.3	0.2
Indane[c]	1036	MS	<0.1	<0.1	<0.1	–	<0.1	–	<0.1
1-Ethyl-3-isopropylbenzene[c]	1047	MS	<0.1	–	–	–	–	–	–
3-Methyl-1-butyl butanoate	1060	MS, RI	<0.1	<0.1	<0.1	0.1	–	<0.1	<0.1
γ-Terpinene	1062	MS, RI	–	–	–	<0.1	<0.1	–	–
1-Octanol	1063	MS, RI	0.1	–	0.1	0.1	<0.1	<0.1	–
1,1,3-Triethoxypropane	1075	MS	0.1	<0.1	0.4	–	0.2	0.1	<0.1
Allyl hexanoate[c]	1080	MS, RI	–	–	–	0.1	–	–	–
Terpinolene	1088	MS, RI	–	–	–	<0.1	–	–	–
p-Cymenene	1089	MS	<0.1	–	–	<0.1	–	<0.1	–
2-Nonanone	1091	MS, RI	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1-Diethoxyhexane	1093	MS	0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Propyl hexanoate	1095	MS, RI	<0.1	–	–	–	–	–	–
Ethyl heptanoate	1097	MS, RI	0.2a	0.2a	0.1a	0.1a	0.2a	0.3a	0.1a

Table 1 (*continued*)

Compound	RI[a]	ID[b]	A	3B	3C	3D	7E	7F	7G
2-Nonanol	1099	MS, RI	–	<0.1	0.1	0.2	<0.1	<0.1	0.1
Nonanal	1102	MS, RI	<0.1	0.1	0.3	0.1	0.1	0.4	0.1
2-Methylbenzofuran	1109	MS	<0.1	–	–	–	–	–	–
2-Phenylethanol	1110	MS, RI	<0.1	–	–	<0.1	–	–	–
Methyl octanoate	1125	MS, RI	–	–	<0.1	<0.1	–	–	–
Ethyl cyclohexanecarboxylate	1129	MS	<0.1	<0.1	–	–	<0.1	<0.1	–
1-Methylindane[c]	1135	MS	–	–	–	–	<0.1	–	<0.1
1,2,3,4-Tetramethylbenzene	1140	MS	–	–	–	–	<0.1	<0.1	–
4-Vinylanisole[c]	1144	MS, RI	0.1	–	–	–	–	–	–
Isobutyl hexanoate	1150	MS, RI	0.1	–	–	–	–	–	<0.1
Menthone[c]	1154	MS, RI	–	–	–	0.1	–	0.1	–
neo-Menthol	1165	MS, RI	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
p-Cresol acetate[c]	1168	MS	<0.1	–	–	–	–	–	–
1,1,6-Trimethyl-1,2,3,5-tetrahydronaphthalene	1169	MS	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethyl benzoate	1170	MS, RI	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Mentol	1173	MS, RI	0.2a	0.2a	0.3a	0.2a	0.2a	0.1a	0.1a
4-Ethylphenol	1175	MS, RI	<0.1	–	–	–	–	–	–
2-Furfuryl-5-methylfuran[c]	1177	MS	0.1	–	<0.1	–	–	–	–
Naphthalene	1179	MS, RI	–	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Octanoic acid	1180	MS, RI	<0.1	–	–	–	–	–	–
(*Z*)-3-Hexenyl butanoate	1186	MS, RI	–	–	–	<0.1	–	–	–
1-Methylene-4,4,7a-trimethyl-3a,4,5,7a-tetrahydroindene[c]	1188	MS	0.1	0.2	0.1	<0.1	0.1	0.1	<0.1
Methyl salicylate	1190	MS, RI	0.5	0.1	<0.1	0.1	0.1	0.1	0.1
Ethyl octanoate	1195	MS, RI	15.2a	18.5a	24.4b	23.9b	20.0b	21.1b	17.4a
Decanal	1204	MS, RI	<0.1	0.1	0.5	0.2	0.2	0.2	0.1
1,6,6-Trimethyl-1,2,3,4-tetrahydronaphthalene	1208	MS	0.1a	0.4a	0.2a	0.1a	0.3a	0.3a	0.1a
Octyl acetate	1214	MS, RI	–	–	–	<0.1	–	–	<0.1
3-Butyl-3-methyl-cyclohexanone[c]	1218	MS	0.1	<0.1	0.1	–	–	<0.1	–
3-*tert*-Butyl-4-hydroxyanisole[c]	1234	MS	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1
Ethyl phenylacetate	1244	MS, RI	<0.1	<0.1	–	<0.1	<0.1	<0.1	<0.1
1,6,8-Trimethyl-1,2,3,4-tetrahydronaphthalene[c]	1255	MS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3-Methyl-1-butyl hexanoate	1256	MS, RI	<0.1	<0.1	0.1	0.1	0.1	<0.1	<0.1
Edulan I[c]	1257	MS	0.6	<0.1	–	–	<0.1	0.1	–
2-Phenylethyl acetate	1259	MS, RI	<0.1	–	<0.1	<0.1	<0.1	<0.1	–
Ethyl salicylate	1267	MS, RI	<0.1	<0.1	<0.1	<0.1	–	<0.1	<0.1
1-Decanol	1272	MS, RI	0.2	–	0.1	0.2	–	–	–
2,2′-Methylenebis[5-methylfuran][c]	1275	MS	0.6	–	–	–	–	–	–
4-Ethyl-2-methoxyphenol	1276	MS, RI	<0.1	–	–	–	–	–	–
(*E*)-Anethole	1282	MS, RI	–	–	–	<0.1	–	–	–
1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene	1284	MS	0.9	0.2	0.2	<0.1	0.2	0.1	<0.1
2-Methylnaphthalene	1285	MS, RI	–	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
cis-β-Methyl-γ-octalactone	1286	MS, RI	–	<0.1	<0.1	<0.1	0.1	0.1	0.1
1,1-Diethoxyoctane[c]	1287	MS	<0.1	–	<0.1	<0.1	–	–	–
Dihydroedulan I[c]	1289	MS	0.1	–	–	–	–	–	–
Propyl octanoate	1291	MS, RI	0.2	<0.1	0.1	–	0.1	0.1	0.1
Menthyl acetate[c]	1293	MS, RI	–	–	–	<0.1	–	–	–
2-Undecanone	1294	MS, RI	–	<0.1	0.1	–	–	<0.1	–
Ethyl nonanoate	1296	MS, RI	0.5	0.5	0.4	0.5	0.4	0.5	0.2
2-Dodecanol	1298	MS	–	<0.1	<0.1	<0.1	–	–	–
Undecanal	1306	MS, RI	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Edulan II[c]	1310	MS	0.9a	0.1b	0.1b	0.1b	0.1b	0.1b	0.1b
Methyl decanoate	1326	MS, RI	–	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2,2-Diethoxyethylbenzene[c]	1329	MS	<0.1	–	–	–	–	–	–
1,2-Dihydro-1,1,6-trimethylnaphthalene	1339	MS	1.0a	0.5b	0.2b	0.1b	0.3b	0.2b	0.2b
Eugenol	1356	MS, RI	–	–	–	<0.1	–	–	0.1
(*E*)-2-Undecenal[c]	1366	MS	–	–	–	–	–	<0.1	<0.1
Ethyl decanoate	1376	MS, RI	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
4-Propyl-2-methoxyphenol[c]	1380	MS, RI	0.2	<0.1	–	0.1	<0.1	<0.1	–
trans-β-Damascenone[c]	1386	MS, RI	0.7a	0.3b	0.3b	0.3b	0.2b	0.2b	0.2b
Ethyl 9-decenoate	1389	MS	0.9a	1.1a	0.6a	0.4a	0.7a	0.5a	1.1a
Benzyl isopentanoate	1392	MS, RI	–	–	–	0.1	–	–	–
Ethyl decanoate	1396	MS, RI	40.5a	40.8a	38.8a	35.3a	38.4a	37.3a	37.6a
Dodecanal	1407	MS, RI	–	0.7a	0.5a	0.4a	0.2b	0.1b	0.1b
1,2-Dimethylnaphthalene	1417	MS	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1

(*continued on next page*)

Table 1 (*continued*)

Compound	RI[a]	ID[b]	A	3B	3C	3D	7E	7F	7G
Dehydroionene	1427	MS	0.3	–	–	–	–	–	–
1,4-Dimethylnaphthalene	1435	MS	–	<0.1	<0.1	–	<0.1	<0.1	<0.1
3-Methyl-1-butyl octanoate	1447	MS, RI	0.7a	0.4a	0.4a	0.4a	0.6a	0.2b	0.6a
2-Methyl-1-butyl octanoate[c]	1450	MS, RI	0.2	0.1	0.1	0.1	0.2	0.1	0.2
Geranyl acetone[c]	1453	MS	–	–	<0.1	–	–	<0.1	–
(*E*)-β-Farnesene	1458	MS, RI	–	–	–	–	<0.1	–	<0.1
1-Dodecanol[c]	1473	MS, RI	–	–	–	<0.1	–	–	–
1,1-Diethoxydecane[c]	1482	MS	–	–	<0.1	–	–	–	–
Propyl decanoate	1493	MS, RI	0.2	0.1	<0.1	0.1	<0.1	<0.1	0.1
Ethyl undecanoate	1495	MS, RI	0.1	0.2	0.1	0.1	0.1	0.1	0.1
2,3,5-Trimethylnaphthalene	1513	MS	–	<0.1	<0.1	–	–	<0.1	<0.1
1,3,6-Trimethylnaphthalene[c]	1520	MS	–	<0.1	<0.1	–	–	<0.1	<0.1
Methyl dodecanoate	1525	MS, RI	–	–	<0.1	<0.1	–	–	<0.1
(1-butylhexyl)-Benzene[c]	1537	MS	<0.1	<0.1	<0.1	–	–	<0.1	0.3
α-Calacorene	1542	MS	0.1	–	–	<0.1	–	–	–
(1-propylheptyl)-Benzene[c]	1550	MS	<0.1	<0.1	<0.1	0.3	–	<0.1	0.2
Butyl decanoate	1557	MS, RI	0.4	0.2	0.1	0.1	0.2	0.1	0.2
(1-ethyloctyl)-Benzene[c]	1559	MS	<0.1	<0.1	<0.1	–	–	–	<0.1
(*E*)-Nerolidol[c]	1564	MS, RI	0.3	0.1	0.1	<0.1	<0.1	0.1	<0.1
Ethyl 9-dodecenoate[c]	1590	MS	–	0.1	<0.1	–	<0.1	<0.1	–
Ethyl dodecanoate	1595	MS, RI	11.9a	10.7a	6.8a	10.5a	10.2a	9.5a	9.6a
1,2-Dihydro-1,5,8-trimethylnaphthalene[c]	1600	MS	0.2	0.7	0.1	0.1	0.2	0.2	0.4
Tetradecanal[c]	1611	MS, RI	–	–	0.1	<0.1	<0.1	<0.1	<0.1
Isopropyl dodecanoate[c]	1621	MS, RI	–	–	0.1	–	–	<0.1	<0.1
(1-pentylhexyl)-Benzenev[c]	1625	MS	–	–	–	<0.1	–	–	<0.1
di-*p*-Tolylmethane[c]	1628	MS, RI	–	–	–	–	<0.1	–	<0.1
(1-butylheptyl)-Benzene[c]	1631	MS	0.1	<0.1	<0.1	–	–	<0.1	<0.1
2-Phenylethyl hexanoate [c]	1639	MS, RI	<0.1	<0.1	–	–	<0.1	<0.1	0.5
(1-propyloctyl)-Benzene[c]	1643	MS	<0.1	–	–	–	–	<0.1	<0.1
3-Methyl-1-butyl decanoate	1660	MS, RI	0.7	0.4	0.3	0.1	0.6	0.2	0.8
2-Methylbutyl decanoate[c]	1663	MS, RI	0.2	0.2	0.1	<0.1	0.2	0.1	0.2
(1-ethylnonyl)-Benzene[c]	1671	MS	<0.1	<0.1	<0.1	–	–	–	–
Cadalene[c]	1681	MS	0.0	0.0	<0.1	<0.1	<0.1	<0.1	0.2
Propyl dodecanoate[c]	1696	MS, RI	<0.1	–	–	–	<0.1	–	0.3
(1-methyldecyl)-Benzene[c]	1704	MS	<0.1	<0.1	–	–	–	–	0.7
(1-pentylheptyl)-Benzene[c]	1711	MS	0.1	<0.1	<0.1	<0.1	–	<0.1	0.7
(1-butyloctyl)-Benzene[c]	1716	MS	<0.1	<0.1	<0.1	<0.1	–	<0.1	<0.1
(*E*,*E*)-Farnesol[c]	1722	MS, RI	<0.1	0.1	–	–	–	0.1	0.3
(1-propylnonyl)-Benzene[c]	1725	MS	–	–	–	0.3	–	–	<0.1
Butyl dodecanoate[c]	1788	MS, RI	0.1	<0.1	–	–	<0.1	–	0.2
(1-Ethyldecyl)-benzene[c]	1790	MS	<0.1	<0.1	<0.1	0.2	–	–	0.1
Ethyl tetradecanoate	1793	MS, RI	0.3a	0.1a	0.1a	0.2a	0.2a	0.1a	0.5a
(1-Pentyloctyl)-benzene[c]	1801	MS	–	<0.1	–	0.2	–	<0.1	<0.1
Propyl tetradecanoate[c]	1804	MS, RI	–	<0.1	–	–	<0.1	<0.1	0.3
(1-butylnonyl)-Benzene[c]	1812	MS	–	<0.1	–	0.1	–	–	<0.1
(*Z*,*E*)-Farnesyl acetate[c]	1818	MS	<0.1	–	<0.1	–	–	<0.1	<0.1
2-Phenylethyl octanoate[c]	1839	MS, RI	<0.1	–	<0.1	–	<0.1	<0.1	0.2
(1-Propyldecyl)-benzene[c]	1843	MS	–	<0.1	–	0.1	–	–	–
Ethyl pentadecanoate	1893	MS, RI	<0.1	–	<0.1	<0.1	<0.1	–	–
Methyl hexadecanoate	1927	MS, RI	–	–	–	–	–	–	<0.1
Ethyl (*Z*)-9-hexadecenoate	1990	MS, RI	<0.1	<0.1	<0.1	<0.1	–	–	–
Ethyl hexadecanoate	1993	MS, RI	0.1	–	<0.1	0.1	<0.1	<0.1	0.1
Isopropyl hexadecanoate[c]	2038	MS, RI	<0.1	–	<0.1	–	<0.1	<0.1	–
2-Phenylethyl decanoate[c]	2039	MS, RI	–	–	<0.1	–	<0.1	–	<0.1
Ethyl linoleate	2152	MS, RI	<0.1	–	–	–	–	–	–
Butyl hexadecanoate	2188	MS, RI	<0.1	–	<0.1	<0.1	<0.1	<0.1	<0.1

A: White cane spirit; 3B, 3C and 3D: 3 year-old rums of three commercial brands; 7E, 7F and 7G: 7 year-old rums of three commercial brands. –: Not detected.

Different letters indicate significant difference at 95% confidence level.

[a] Retention index on SPB-5 column.

[b] ID = Identification: MS, identified on basis of mass spectral data alone; MS, RI, identified on the basis of both mass spectral and GC retention index data.

[c] Compound reported for the first time in rum.

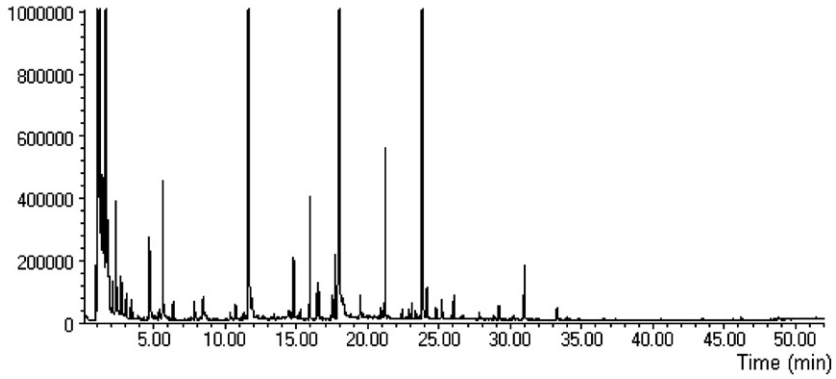

Fig. 3. GC–MS chromatogram of 7 years-old rum extracted by headspace SPME.

esters, though some methyl, 3-methyl-1-butyl, 2-methyl-1-butyl and phenyl esters (among others) were also detected. Esters are products of yeast metabolism or are formed during the aging process (maturation) by esterification of fatty acids in the presence of ethanol at high concentration (Nykänen & Nykänen, 1983, 1991). Undoubtedly also present, largely as a result of fermentation, were many of the 14 alcohols, 9 aldehydes, 6 ketones and 3 acids detected in the extracts. In total, 10 acetals were identified, presumably formed during distillation by a reaction of the alcohol with an aldehyde (Nykänen & Nykänen, 1983, 1991).

The approximately 47 benzenic compounds, 16 terpenoids, 6 phenols, 6 furans and 3 benzopyrans detected are presumably derived from the oak wood. Among the volatiles released from the oak, and from a sensory point of view the most important compounds, are *cis*- and *trans*-β-methyl-γ-octalactone, commonly known as the oak or whisky lactones (Nykänen & Nykänen, 1991). Only the *cis* isomer was detected in all rum samples.

Comparing the data of white cane spirit with the rums, there are only minor differences between them, excepting those observed for ethyl acetate, isobutanol, ethyl isobutanoate, 3-methylphenol, 2-furfural, (*Z*)-3-hexenol, *o*-xylene, benzaldehyde, 2-nonanone, 2-nonanol, 2-methylbenzofuran, 4-vinylanisole, 1,1,6-trimethyl-1,2,3,5-tetrahydronaphthalene, 4-ethylphenol, naphthalene, octanoic acid, methyl salicylate, edulan I, 2,2′-methylenebis[5-methylfuran], 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene, 2-methylnaphthalene, *cis*-β-methyl-γ-octalactone, dihydroedulan I, propyl octanoate, edulan II, *trans*-β-damascenone, dodecanal, dehydroionene and butyl decanoate. The origin of some of them, e.g., 2-furfural, benzaldehyde, and *cis*-β-methyl-γ-octalactone, is the oak wood during maturation, while others could be added to rum from the ethanol used in the preparation of the final product.

In this study, six samples of four brands of Cuban rums were investigated. Three samples were labelled as 3 years-old and the other three as 7 years-old. In all of them, ethyl esters, 3-methyl-1-butanol and 2-methyl-1-butanol were the major components found. The ethyl ester profiles were similar in all samples and suggest that the ethyl ester profiles are affected by both, yeast metabolism and distillation protocol, but not by maturation. In general, no significant differences were found between individual compounds detected in rum samples, except for ethyl acetate and benzaldehyde.

Principal component analysis was used in order to show patterns between aged rums. In Fig. 3 shows the scores of the three first principal components which explain 90% of the total variance. There are two groupings, corresponding to rums with 3 and 7 years old. The variables more correlated with the first principal component will allow differentiation of the two types of aged rums. The first principal component, which explains 69% of the total variance, is highly correlated with ethyl acetate, acetic acid, diethoxymethane, ethyl butanoate, benzaldehyde, limonene, menthol, 3-*tert*-butyl-4-hydroxyanisole, 2-dodecanol, *trans*-β-damascenone and dodecanal. It is interesting to note that these compounds are not produced directly from the interaction with oak wood, but some of them were significantly different among the samples and other showed a tendency to be different between the two maturation ages. The second principal component (14.1% of the total variance) is highly correlated with 1,1-diethoxy-2-methylpropane, whereas acetaldehyde concentration contributes more strongly to the third principal component which explains a further 6.9% of the total variance.

4. Conclusions

Headspace solid-phase microextraction is a very simple and fast technique for analyzing volatile compounds in rums. The interference of a high ethanol content was resolved by a dilution of the sample to 12% v/v of ethanol. The extraction procedure using a 100 μm PDMS fibre with 35 min at 30 °C, permitted the isolation of a large quantity of volatile compounds. A total of 184 constituents were identified in the SPME extracts, sixty-eight of which are reported for the first time in rum. Semi-quantitative analysis, based on area percent, showed very good reproducibility. With the use of standard calibration curves, the method can be easily applied to measure absolute concentrations. The use of only 15 volatile compounds permits discrimination between the 3 and 7 years-old rums.

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