ANALYSIS OF VOLATILE COMPOUNDS IN CHINESE NANJING MARINATED DUCK MEATS USING VARIOUS POLARITY SPME FIBRES AND GC COLUMNS

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***Abstract*—The main volatile compounds of Chinese Nanjing marinated duck meats were studied using SPME-GC/MS. There were 25 volatile compounds (alkanes, aldehydes, kenones, alcohols, N-containing and benzezes, furan, acids, esters alkenes) identified and quantified based on a bipolar fiber 75μm CAR-PDMS using a non-polar DB-5 (30 m × 0.25 mm i.d.) column and 21 volatiles detected based on a moderate polar fiber 50/30μm CAR/DVB/PDMS using a DB-innowax (30 m × 0.25 mm i.d.) column.**

***Index Terms*—Volatile compounds, Chinese Nanjing marinated duck meat, SPME, GC-MS.**

I. INTRODUCTION

Chinese Nanjing marinated duck is a traditional meat product in China and its flavours (volatile & non-volatile) are highly desired. There has been much research aimed at analysing volatiles using many chemical methods such as SPME (solid-phase microextraction), NPSD (nitrogen purge-and-steam distillation), SDE (simultaneous distillation/extraction), followed by quantitative and qualitative analysis of the volatile compounds present using GC-MS techniques. (Soncin, Chiesa, Cantoni, & Biondi, 2007).

Liu, Xu, Ouyang, & Zhou, 2006 carried out a primary analysis on the volatile compounds of Chinese Nanjing duck meat, extracted with a bipolar fiber 75μm (CAR-PDMS) SPME fiber (Supelco) and the separated on a non-polar DB-5-MS column (60 m × 0.32 mm i.d.) and they tentatively identified about 92 volatile compounds, (including hydrocarbons, aldehydes, and alcohol). However, because of the SPME procedures and column type used in that study, they were only able to examine the non-polar volatile compounds originating from the duck meat. Therefore, in order to investigate the whole range of polar and non-polar volatile compounds we have undertaken a similar investigation but have used a variety of SPME fibres (having various polarities) and GC-MS columns to cover the entire range of expected compounds.

II. MATERIALS AND METHODS

1.1.Material

Chinese Nanjing marinated ducks were purchased at Wal-Mart supermarket Nanjing, Four gram of breast and leg meats, trimmed of subcutaneous fat, were individually minced and then mixed (1:1; w/w), and placed in a 15mL headspace vial (Thermo), and stored at -20℃until further use.

1.2.Headspace solid-phase microextraction–gas

Chromatography-mass spectrometry (headspace-SPME-GC-MS)

1.2.1.SPME sampling

SPME fibers were directedly inserted into sample vials and allowed to equilibrate at 60℃ in a water bath for 40min. Analysis of each sample was repeated twice. Extraction fibers of the bipolar type, CAR/PDMS (75μm thickness) were applied to a DB-5 (non-polar) column whereas the moderately polar fibers, CAR/DVB/PDMS (50/30μm thickness) were applied to a DB-innowax (polar) column.

1.2.2. Gas chromatography–mass spectrometry

Analyzes were performed using a Finnigan Trace GC-MS (Finnigan, U.S.A.). Volatiles were separated using a bonded phase fused silica capillary column DB-5 (30m×0.25mm i.d.) and also on a bonded phase polyethylene glycol fused capillary column DB-innowax (30m×0.25mm i.d.). The SPME fibers were thermally desorbed at 230℃ for 120 s in the injector port (splitless mode). For the DB-5 capillary column, the temperature was as follows: isothermal for 4 min at 35℃ ; increased to 100℃ at a rate of 5℃/min; increased to 200℃ at a rate of 15℃/ min; held for 4 min; increased to 250℃ at a rate of 15℃/ min, and, finally held at 250℃ for 10 min. For the DB-innowax polar column, the temperature program was as follows: isothermal for 4 min at 35℃; increased to 100℃ at a rate of 5℃ /min; increased to 200℃ at a rate of 15℃/ min; held for 4 min; increased to 220℃ at a rate of 15℃/ min, and finally held at 220℃ for 10 min. The transfer line to the mass spectrometer was maintained at 250℃. Mass spectra were obtained using a mass selective detector by electronic impact at 70 eV, a multiplier voltage of 1753 V, and collecting data at a rate of 1 scan s-1 over the m/z range of 33–450 u.m.a. Compounds were tentatively identified by comparing their mass spectra with

those contained in the Nist05 and Wiley275, Mainlab libraries and by comparison of their LRI with those reported in the literature (Ai-Nong & Bao-Guo, 2005).

III. RESULTS AND DISCUSSION

The fibers such as 75µm CAR/PDMS and 100µm PDMS are non-polar/ bipolar fibers whereas 50/30µm CAR/DVB/PDMS and CAR/DVB are moderate polar and 85µm PA is a polar fiber. We therefore selected the fibre type to extract the targeted volatiles (De Jager, Perfetti, & Diachenko, 2008). In this paper, we examined the different fibers (75µm CAR/PDMS,50/30µm CAR/DVB/PDMS and 85µm PA) and DB-5 columns, and found that the total area counts of all volatiles in duck meat was highest with the 75µm CAR/PDMS, followed by 75µm CAR/PDMS, 50/30µm CAR/DVB/PDMS and lowest in 85µm PA based on a DB-innowax column. The numbers of volatiles in the descending order were 85µm PA>50/30µm CAR/DVB/PDMS>75µm CAR/PDMS. Therefore the main volatiles in duck meat we examined were non-polar volatiles, and polar-volatiles were just a small part of total volatiles.

From preliminary experimental data, we found that the main non-polar and polar volatiles in duck meat were optimally extracted and detected when using the following conditions: 40min extraction time, 60 C extraction temperature, when using the SPME fibres identified, and is similar to that reported by others (Waldemar, Magdalena, & Janusz, 2004).

Using a combination of the 75µm CAR/PDMS fiber and DB-5 column, we found approximately 25 volatiles (alkanes, aldehydes, ketones, alcohols, esters, acids, alkenes, N-containing compounds) were extracted and seperated (Table 1). When using a combination of the 50/30µm CAR/DVB/PDMS fiber and DB-innowax column we found about 21 volatiles present including a furan (2-pentyl-furan). From this component table, the total area counts of volatiles was higher in DB-5 column compared with DB-innowax column. Aldehydes, which significantly impact on total volatiles as a result of their low odor thresholds, comprised a large proportion of total volatiles. These included, hexanal, pentanal, heptanal, octanal and decanal resulting from auto-oxidation of fatty acids and contribute mainly rancid, green, fresh, cured ham-like flavours. Alcohols such as 1-octen-3-ol, have been considered as one of the active aroma compounds originating from Strecker degradation reactions. The main ketones detected were 2-heptanone, 6-methyl-2-heptanone, 2,3-octanedione) which are nomally aroma volatiles associated with blue cheeses, as a result of microbial formation. Ethyl acetate was the major main ester present, and is considered to result from microbial activity (Meynier, Novelli, Chizzolini, Zanardi, & Gandemer, 1999). Hexanoic acid was the major acid detected in duck meat and has also found in Iberian hams. D-Limonene and ethyl benzene were the main alkanes and benzenes present and they have been reported as contributing to fat rancidity in ducks as a result of accumulation from feeding. 2-Pentyl-furan was the only furan detected in duck meat which is likely originated by Maillard reaction, contributing to sweet, burnt and sugar notes (Sánchez-Peña, Luna, García-González, & Aparicio, 2005).

IV. CONCLUSION

The profile of volatiles contributing to the characteristic flavour of Nanjing duck was determined using a bipolar extraction fibre (75µm CAR/PDMS) with a non-polar DB-5 column and a moderate polarity extraction fibre (50/30µm CAR/DVB/PDMS) with a polar DB-innowax column. The results showed that the non-polar volatiles were the main volatiles present, but a small number of polar volatiles were also found in duck meat. It is therefore essential to use both polar and non-polar systems for the detection of flavor volatiles. Altogether we detected furan (1), alkanes (3), aldehydes (16), ketones (11), alcohols (11), esters (6), acids (5) and alkenes (19) in duck meat. Some of these volatiles were not repoted by (Liu et al, 2006), probably because of the different extraction and separating methods used.

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Table 1.The main volatile compounds were analyzed using a bipolar fiber 75µm CAR/PDMS with a non-polar DB-5 column, and polarity fibre,50/30µm CAR/DVB/PDMS, with a polar DB-innowax column

Volatiles	[A]LRI	Identification	DB-5 ($\times 10^8$)	DB-innowax ($\times 10^8$)	[D]T ($\times 10^8$)
Alkanes					
Octane	844	[B]MS, LRI	2.43	[C]nd	2.43
Aldehydes					
3-Methyl-butanal	816	MS, LRI	0.18	nd	0.18
Pentanal	935	MS, LRI	196.65	13.39	210.04
Hexanal	933	MS, LRI	78.64	344.17	422.81
Heptanal	916	MS, LRI	41.0	nd	41.0
Benzaldehyde	936	MS, LRI	4.18	2.84	7.02
Octanal	957	MS, LRI	25.8	nd	25.8
Nonanal	930	MS, LRI	Nd	198.70	198.70
2-Octenal	900	MS, LRI	Nd	1.17	1.17
5-Ethylcyclopent-1-enecarboxaldehyde	849	MS, LRI	1.23	1.07	2.3
2-Octanal	847	MS, LRI	0.72	nd	0.72
(Z)-7-Hexadecenal	843	MS, LRI	0.34	nd	0.34
Ketone					
2-Butanone	916	MS, LRI	1.45	nd	1.45
2-Heptanone	869	MS, LRI	9.50	nd	9.50
6-Methyl-2-heptanone	804	MS, LRI	1.21	nd	1.21
2,3-Octanedione	953	MS, LRI	37.14	81.79	118.93
3-Octanone	855	MS, LRI	Nd	0.62	0.62
1-Octen-3-one	837	MS, LRI	Nd	0.52	0.52
Alcohols					
1-Pentanol	925	MS, LRI	33.3	4.40	37.70
1-Hexanol	805	MS, LRI	Nd	1.57	1.57
1-Octen-3-ol	900	MS, LRI	17.82	27.35	45.17
2-Octen-1-ol	837	MS, LRI	1.63	nd	1.63
2-Ethyl-1-hexanol	917	MS, LRI	Nd	1.83	1.83
1-Octanol	934	MS, LRI	Nd	2.07	2.07
Esters					
Ethyl Acetate	906	MS, LRI	443.94	144.30	588.24
1-Propen-2-ol, acetate	762	MS, LRI	44.39	nd	44.39
Acids					
N-Methyltaurine	809	MS, LRI	31.9	nd	31.9
Hexanoic acid	846	MS, LRI	Nd	2.71	2.71
Alkenes					
p-Xylene	842	MS, LRI	11.47	8.63	20.1
1R-à-Pinene	831	MS, LRI	1.11	nd	1.11
D-Limonene	755	MS, LRI	1.06	nd	1.06
Naphthalene	854	MS, LRI	0.36	nd	0.36
N-containing and benzene compounds					
Ethylbenzene	879	MS, LRI	3.08	nd	3.08
Ethanolamine	954	MS, LRI	Nd	6.50	6.50
methyl-Benzene	952	MS, LRI	Nd	8.19	8.19
1,2-dimethyl-Benzene	832	MS, LRI	Nd	2,06	2.06
Furans					
2-pentyl-Furan	830	MS, LRI	Nd	2.84	2.84

[A]LRI calculated for a DB-5 and a DB-innowax column. [B]MS: mass spectrum tentatively identified using Nist05, Wiley275, Mainlab libraries. [C]nd: not detected. [D]T: total area counts based on 2 columns.

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