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Simultaneous Gas Chromatography Analysis of Preservatives in Chinese Traditional Meat Products Collected from Ilan County

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ABSTRACT

To assay the hygienic safety data of traditional Chinese meat products, a total of 61 samples including cured duck meat (26), cured pork meat (19) and cured pork liver (14) were collected from conventional markets and supermarkets in Ilan County, Taiwan. They were simultaneously analyzed for 10 preservatives by gas chromatography with non-polar DB-1 Megabore column and flame ionization detector. Only the legal preservatives sorbic acid and benzoic acid were found, while illegal preservatives in meat products, including dehydroacetic acid and 7 esters of ρ-hydroxybenzoic acid, were not. The ratio of sample detected to contain sorbic acid and benzoic acid was 54.0% and 8.1%, respectively, of the total samples. The level of sorbic acid and benzoic acid in these samples ranged from <10 to 2,130 ppm and <10 to 933 ppm, respectively. One sample of cured pork meat contained sorbic acid at more than 2,000 ppm, the allowable limit. All the other samples were less than this allowable limit. The level of sorbic acid and benzoic acid detected in samples collected from conventional markets was less than that from supermarkets. Incorrect labeling of food products was more common in traditional markets than in supermarkets. Preservatives were not misused in the traditional cured meats, but the labeling was a problem.

Key words: cured meat products, preservatives, sorbic acid, benzoic acid, Ilan

INTRODUCTION

Chinese traditional cured duck meat, cured pork meat, and cured pork liver are popular foods in Taiwan. These products are produced in Ilan County by a series of processes including salting, dressing and drying. Preservatives are usually added for inhibiting bacterial growth in these products. In Taiwan, sorbic acid, benzoic acid, dehydroacetic acid and 7 esters of ρ-hydroxybenzoic acid are allowed to use in food. However, each preservative has an allowable limit, e.g. sorbic acid 2.0 g/kg and benzoic acid 1.0 g/kg(1). Their applicable products are also regulated. For example, the preservatives used in meat products are sorbic acid and benzoic acid.

Some methods have been developed for determining preservatives in food. A traditional method for determination of benzoic acid is based on reacting with iron chloride to form an iron benzoate precipitate to form a red color(2). Benzoic acid may also be quantified by a modified Mohler method using alkaline titration(3). Sorbic acid is usually quantified using a spectrophotometric method measuring the absorbance at 530 nm(3,4). This method detects a red complex formed by the reaction of thiobarbituric acid with malonaldehyde, which is produced when sorbic acid is oxidized by $K_2Cr_2O_7$. The above methods, however, are complex in operation and subject to interference. The analytical techniques have been much improved by using spectrophotometry(5), thin layer chromatography (TLC)(6), gas chromatography (GC)(7,8), high performance liquid chromatography (HPLC)(9,10) and GC-mass spectrophotometry(11,12). Among these methods, GC can provide an analysis with good resolution as well as excellent sensitivity and is one of the most important analytical techniques. Hence, the GC method is recognized as an official method by many countries(2).

In Taiwan, cured duck meat, cured pork meat and cured pork liver are sold at traditional markets and supermarkets in Ilan County. To establish hygienic safety data, the residues of preservatives in these products collected from traditional markets and supermarkets were analyzed using GC method. Labeling, including manufacturer, expiring date, and food additives in these products, was also examined.

MATERIALS AND METHODS

I. *Materials*

A total of 61 samples of cured duck meat(26), cured pork meat(14) and cured pork liver(21) were collected from 53 vendors in 10 districts of Ilan County. Nineteen samples were collected from conventional markets and the other samples were from supermarkets. The labeling of these samples was examined. All samples were then homogenized with a cutter and a blender and immediately stored at -20˚C until use.

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Benzoic acid (BA) was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Sorbic acid (SA), dehydroacetic acid (DHA), methyl ρ-hydroxybenzoate (MP), ethyl ρ-hydroxybenzoate (EP), propyl ρ-hydroxybenzoate (PP), butyl ρ-hydroxybenzoate (BP) were obtained from Fluka Chemicals Co. (Buchs, Switzerland). Isopropyl ρ-hydroxybenzoate (Iso-PP), isobutyl ρ-hydroxybenzoate (Iso-BP), sec-butyl ρ-hydroxybenzoate (Sec-BP) were products of Kogyo Chemicals Co. (Tokyo, Japan). Other reagents including diethyl ether, acetone, tartaric acid, sulfuric acid, hydrochloride, sodium chloride, sodium hydroxide, sodium hydrogen carbonate, anhydrous sodium sulfate and silicon resin were purchased from E. Merck (Darmstadt, Germany).

II. *Preparation of Standard Solutions*

One hundred mg of SA, BA, DHA, MP, EP, Iso-PP, PP, Sec-BP, Iso-BP and BP were weighed separately and dissolved in 100 mL of acetone as standard solution. The standard solution was diluted to a series of concentrations ranging from 0.2 to 6.0 μg/mL for use.

III. *Sample Preparation*

The procedure of sample preparation was according to the method for preservatives in food[13]. Each sample of 30 g mixed cured duck meat, cured pork meat and cured pork liver was neutralized with 10% sodium hydroxide or 10% hydrochloride in a 100-mL beaker. This neutral solution was then transferred into a 500-mL round-bottomed flask containing 15 mL of 15% tartaric acid, 60 g sodium chloride and one drop of silicon resin. The solution was then diluted with water to the volume of 200 mL and steam-distilled at a rate of 10 mL/min. Fifty mL of distillate was transferred to a separation funnel, acidified with 10% sulfuric acid, saturated with sodium chloride, and extracted with 100 mL (2 X) of diethyl ether. The combined diethyl ether layer was washed with 30 mL of saturated sodium chloride solution, added with anhydrous sodium sulfate to make free the solution of water, and then filtered through a Toyo No.2 filter. The filtrate was evaporated under vacuum to dryness. The residue was then added with acetone to a volume of 5 mL for GC determination.

IV. *Recovery Test*

Thirty g each of cured duck meat, cured pork meat and cured pork liver was spiked with 250 and 500 μg of each preservative and mixed well. The sample was extracted using the procedure of sample preparation described above and then subjected to GC analysis. The analysis of each fortification was carried out in triplicate and the sample blank unspiked with standards was also performed.

V. *GC Conditions*

A Perkin Elmer GC autosystem equipped with FID, hydrogen and air flow at 30 and 300 mL/min, respectively, was used in this study. The temperature of detector and injection port was 250˚C. Separation column was DB-1 Megabore column packed with 100% dimethyl polysiloxane (0.53 mm x 30 m, 0.5 μm film thickness, J & W Scientific Co., USA). The oven temperature was set at 105˚C for 7 min, raised to 160˚C at 10˚C/min, and then kept 160˚C for 2.5 min. The injection volume was 1 μL in this study.

RESULTS AND DISCUSSION

The labeling situation of all samples collected from conventional markets and supermarkets is shown in Table 1. The ratio of incorrect labeling on expiration date was 84% of samples from conventional markets and 7% from supermarkets. The ratio of incorrect labeling samples on food additive was 74% for conventional markets and 7% for supermarkets. The ratio of non-vacuum package samples was 89% for conventional markets and 5% for supermarkets. It indicated that the incorrect labeling in cured duck meat, cured pork meat and cured pork liver sold at conventional markets was a serious problem.

Using a non-polar DB-1 Megabore column and GC conditions as described above, the standards of SA, BA, DHA, MP, EP, Iso-PP, PP, Sec-BP, Iso-BP and BP were found to appear at 1.51, 2.34, 5.07, 8.64, 10.14, 10.74, 11.79, 12.26 and 13.33 min, respectively, as shown in Figure 1. The typical GC chromatograms of test samples of cured duck meat, cured pork meat and cured pork liver are shown in Figure 2. The peak of each preservative was symmetric, sharp and of

Table 1. The ratio of mislabeled samples in cured duck meat, cured pork meat and cured pork liver

Product	Sample number		Non-vacuum package		Expiring date		Food additive	
	Traditional market	Super-market	Traditional market	Super-market	Traditional market	Super-market	Traditional market	Super-market
Cured duck meat	2	24	2[a] (100%)[b]	0	2 (100%)	1 (4%)	0 (13%)	3
Cured pork meat	12	9	11 (92%)	1 (11%)	10 (83%)	1 (11%)	10 (83%)	0
Cured pork liver	5	9	4 (80%)	1 (11%)	4 (80%)	1 (11%)	4 (80%)	0
Total	19	42	17 (89%)	2 (5%)	16 (84%)	3 (7%)	14 (74%)	3 (7%)

[a]: Sample number of non-vacuum package and incorrect sample number for expiring date and food additive.
[b]: The ratio of non-vacuum package and incorrect labeling samples.

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good resolution. This method allows one sample to be analyzed in 14 min. Lin and Choong[14] developed another GC method with a medium polar CP SIL 8 CB column that analyzed preservatives in 25 min. Our GC method was more rapid than that of Lin and Choong[14].

The standard curves of preservatives were made by plotting serial concentrations of standard solution versus their responses based on the peak area of GC chromatogram. In the range of 0.2~6.0 μg/mL, a relationship between each preservative concentration and peak area was linear (Table 2). Each correlation coefficient (r) was 0.99.

The recoveries of 10 preservatives tested from cured duck meat, cured pork meat and cured pork liver are listed in Table 3. The recoveries of the 10 preservatives spiked with 250 and 500 μg were in the range of 77.8~88.6% and 82.3~95.2%, respectively. The recovery for each preservative was better in samples spiked with 500 μg. The average recoveries of the 10 preservatives were in the range of 80.1~91.9%, and were used to calculate the actual amount of preservative in the sample in this study.

The levels of preservatives in the 61 samples of cured duck meat, cured pork meat and cured pork liver are shown in Table 4. Sorbic acid and benzoic acid were the only two preservatives found in these meat products. The range of sorbic acid and benzoic acid in these meat products was <10~2,130 mg/kg and <10~933 mg/kg, respectively. The detected ratio of sorbic acid and benzoic acid in these meat products was 54.0% and 8.1%, respectively. Only one sample of cured pork meat contained 2.13 g/kg sorbic acid, all the other samples compiled to the regulations on the allowable limit being 2.0 g/kg for sorbic acid and 1.0 g/kg for benzoic acid[1]. Hence, 98.3% of these products properly used food additives. In addition, meat products collected from conventional markets were higher in sorbic acid and benzoic acid than those from supermarkets. In general, the level of sorbic acid was higher than benzoic acid in these meat products, especially for cured pork meat.

In this study, a rapid and sensitive GC method was developed to simultaneously analyze the preservatives in meat products. Sorbic acid and benzoic acid were used legally in Chinese products of cured duck meat, cured pork meat and cured pork liver, other illegal preservatives were not detected similar to a previous report[15]. However, the incorrect labeling in these meat products is a problem.

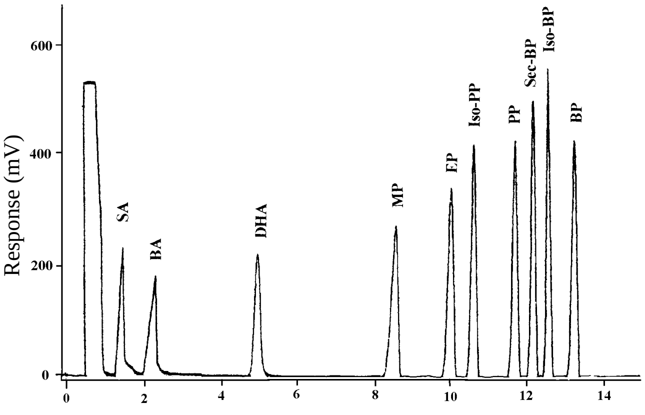

Figure 1. GC chromatogram of 10 standard food preservatives. The amount of each food preservative was 1 μg.

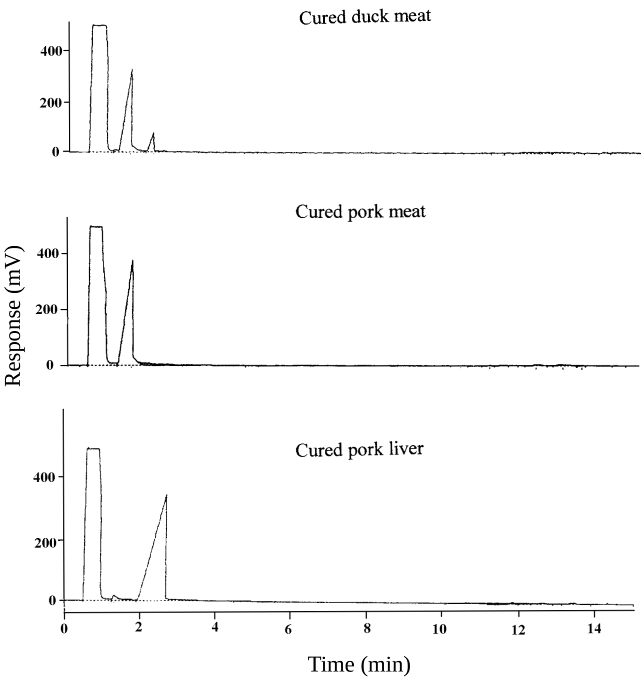

Figure 2. Typical GC chromatograms of tested samples of cured duck meat, cured pork meat and cured pork liver.

Table 2. Linear regression equation[a] and correlation coefficients for authentic preservatives

Preservatives	Slope (a)	Intercept (b)	Coefficient (r)
SA (Sorbic acid)	2134.5	-95627	0.9986
BA (Benzoic acid)	2366.1	-221672	0.9924
DHA (Dehydroacetic acid)	2060.2	-50299	0.9992
MP (Methyl ρ - Hydroxybenzoate)	2718.6	-13915	0.9994
EP (Ethyl ρ - Hydroxybenzoate)	2849.5	-18738	0.9993
Iso-PP (Isopropyl ρ - Hydroxybenzoate)	2954.1	-19531	0.9992
PP (Propyl ρ - Hydroxybenzoate)	3015.2	-24637	0.9991
Sec-BP (Secbutyl ρ - hydroxybenzoate)	3142.2	-21272	0.9997
Iso-BP (Isobutyl ρ - Hydroxybenzoate)	3169.4	-1978.7	0.9998
BP (Butyl ρ - Hydroxybenzoate)	3178.5	+23373	0.9998

[a]: Y = aX + b, where Y = relative peak area and X = amount of preservative (μg) analyzed by GC.

Table 3. Recovery rates of preservatives in cured meat, cured pork meat and cured pork liver spiked with food preservatives

Product	Preservatives	amount (μg) spiked		Average
		500	250	
Cured duck meat	SA (Sorbic acid)	95.2 ± 1.3	88.6 ± 2.2	91.9
	BA (Benzoic acid)	93.4 ± 1.5	86.9 ± 2.1	90.2
	DHA (Dehydroacetic acid)	93.8 ± 1.7	87.3 ± 1.9	90.6
	MP (Methyl ρ - hydroxybenzoate)	86.5 ± 2.1	79.5 ± 2.3	83.0
	EP (Ethyl ρ - hydroxybenzoate)	89.3 ± 1.9	81.4 ± 1.7	85.4
	Iso-PP (Isopropyl ρ - hydroxybenzoate)	90.6 ± 1.8	80.6 ± 2.1	85.6
	PP (Propyl ρ - hydroxybenzoate)	91.7 ± 1.7	79.5 ± 1.8	85.6
	Sec-BP (Secbutyl ρ - hydroxybenzoate)	90.4 ± 1.6	79.4 ± 2.4	84.9
	Iso-BP (Isobutyl ρ - hydroxybenzoate)	86.2 ± 1.7	78.6 ± 1.7	82.4
	BP (Butyl ρ - hydroxybenzoate)	89.5 ± 1.5	79.8 ± 1.5	84.7
Cured pork meat	SA (Sorbic acid)	93.5 ± 1.5	86.5 ± 1.7	90.0
	BA (Benzoic acid)	91.9 ± 1.7	84.7 ± 1.6	88.3
	DHA (Dehydroacetic acid)	90.5 ± 1.6	84.5 ± 1.8	87.5
	MP (Methyl ρ - hydroxybenzoate)	84.9 ± 1.4	78.7 ± 1.7	81.8
	EP (Ethyl ρ - hydroxybenzoate)	88.4 ± 1.6	80.5 ± 1.6	84.5
	Iso-PP (Isopropyl ρ - oxybenzoate)	86.3 ± 1.5	81.7 ± 1.8	84.0
	PP (Propyl ρ - hydroxybenzoate)	89.8 ± 1.5	83.1 ± 1.5	86.5
	Sec-BP (Secbutyl ρ - hydroxybenzoate)	87.6 ± 1.7	80.7 ± 1.8	84.2
	Iso-BP (Isobutyl ρ - hydroxybenzoate)	85.9 ± 1.9	79.5 ± 1.5	82.7
	BP (Butyl ρ - hydroxybenzoate)	90.2 ± 1.7	79.1 ± 1.9	84.7
Cured pork Liver	SA (Sorbic acid)	88.9 ± 1.8	83.5 ± 2.1	86.2
	BA (Benzoic acid)	89.3 ± 1.6	82.2 ± 1.6	85.8
	DHA (Dehydroacetic acid)	89.8 ± 1.9	83.3 ± 1.5	86.6
	MP (Methyl ρ - hydroxybenzoate)	83.3 ± 1.8	78.2 ± 1.8	80.8
	EP (Ethyl ρ - hydroxybenzoate)	84.2 ± 1.7	79.6 ± 1.9	81.9
	Iso-PP (Isopropyl ρ - oxybenzoate)	83.7 ± 1.9	78.7 ± 1.4	81.3
	PP (Propyl ρ - hydroxybenzoate)	82.6 ± 1.5	77.9 ± 1.9	80.2
	Sec-BP (Secbutyl ρ - hydroxybenzoate)	83.2 ± 1.8	78.5 ± 1.3	80.9
	Iso-BP (Isobutyl ρ - hydroxybenzoate)	82.3 ± 2.1	77.9 ± 1.5	80.1
	BP (Butyl ρ - hydroxybenzoate)	84.2 ± 1.7	78.2 ± 1.9	81.3

Table 4. Levels of food preservatives in cured duck meat, cured pork meat and cured pork liver collected from Ilan County

Product	Sorbic acid (ppm)		Benzoic acid (ppm)		Other food peservatives[a]	
	Traditional market	Super-market	Traditional market	Super-market	Traditional market	Super-Market
Cured duck meat	ND[b]	ND~870	ND	ND~345	ND	ND
		(297 ± 64)[c]		(39 ± 19)		
Cured pork meat	ND~807	ND~2,130	ND~46	ND~52	ND	ND
	(139 ± 86)	(1,070 ± 283)	(8 ± 4)	(18 ± 7)		
Cured pork liver	ND~440	ND~750	ND~50	ND~933	ND	ND
	(92 ± 87)	(248 ± 82)	(10 ± 10)	(148 ± 105)		

[a]: Other food preservatives include dehydroacctic acid, methyl ρ - hydroxybenzoate, ethyl ρ - hydroxybenzoate, isopropyl ρ - hydroxybenzoate, propyl ρ - hydroxybenzoate, sec-butyl ρ - hydroxybenzoate, isobutyl ρ - hydroxybenzoate and butyl ρ - hydroxybenzoate.

[b]: ND: less than 10 ppm (not detected).

[c]: Data (mean ± S.E.) were calculated based on the assumption that level of not detected sample was zero.

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利用氣相層析法同步分析宜蘭地區傳統畜產品之防腐劑

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摘　要

為了解宜蘭地區市售傳統名產畜產品鴨賞、膽肝和臘肉中防腐劑之含量，分別自宜蘭縣10個鄉鎮市53個不同販賣點採樣，共自傳統市場和超級市場分別採得19和42件樣品，其中鴨賞26件、臘肉14件和膽肝21件，經以氣相層析儀配合DB-1-Megabore層析管分析10種防腐劑，發現產品僅檢出含有食品防腐劑己二烯酸和苯甲酸二種，其他不得在肉製品使用之防腐劑如去水醋酸和七種對羥甲酸酯類均未檢出（<10 ppm）。己二烯酸和苯甲酸在產品中之檢出率分別54.0%和8.1%，檢出濃度分別為<10-2,130 ppm和<10-933 ppm，其中僅一件臘肉中己二烯酸含量2,130 ppm超過合法限量2,000 ppm。另外，傳統市場產品中之防腐劑含量較超市者為低，然而產品不正確標示之比率，則傳統市場產品較超市者為高。顯示宜蘭地區市售名產中防腐劑之違規使用並不嚴重，但是產品之標示尚待加強輔導。

關鍵詞：鹽漬肉製品，防腐劑，己二烯酸，苯甲酸，宜蘭