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Effects of various oils on volatile compounds of deep-fried shallot flavouring

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Abstract

Shallot slices were heated with soybean, corn oils, lard or medium-chain triglycerides (MCT) at 150–160°C for 5 min and the volatiles of deep-fried shallot flavourings were studied. MCT-shallot flavouring, with 17 compounds, was evidently different from other shallot flavourings, with 28 compounds. Total amounts of volatiles were in the order of 70.2, 56.8, 43.6 and 23.3 mg kg^{-1} for lard-, corn oil-, MCT- and soybean oil-shallot flavourings, respectively. Sulphur- and nitrogen-containing compounds, which were the characteristic flavours of deep-fried shallot flavourings, were remarkably high in MCT-shallot flavouring. Lard-shallot flavouring contained, predominantly, oxygen-containing compounds. Soybean oil- and corn oil-shallot flavourings were similar in their profiles but varied in total amounts. MCT-shallot flavouring had a much lighter aroma due to lower amounts of oxygen-containing compounds, and a much less rancid note. Therefore, the use of MCT as a frying oil can providing a shallot flavouring product with better acceptability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Shallot flavouring; Volatile compounds; Soybean oil; Lard; Corn oil; Medium-chain triglycerides

1. Introduction

Shallot (*Allium cepa* L. var. *aggregatum*) is one of the important seasoning spices in Chinese foods. Initially, shallots were crushed and cut into pieces, and then the slices were put into the deep-frying oil at high temperature until the typical shallot flavour was produced. After being deep-fried, the shallots were then taken out of the oil for the application to Chinese cuisine such as instant noodles, fried noodles, fried rice, and rice with ground pork. The volatile compounds of raw, baked, and deep-fried shallot flavourings had been identified by Wu, Chou, Chen and Wu (1982) and reviewed by Fenwick and Hanley (1985), Ho, Zhang, Shi and Tang (1989), and Maarse and Visscher (1989). In the volatiles of deep-fried shallot flavourings, sulphides, disulphides, trisulphides and thiophenes were found to be the major components.

Chan, Liou and Wu (1991) used the methods of short-path distillation, followed by acidic, alkaline and neutral fractionation, to separate the volatiles of deep-fried shallot flavourings. Volatiles from the acidic, alkaline and neutral fractions included sulphides, pyrroles and compounds from the degradation of lipid. The lipid-degraded compounds were identified as (*E*)-2-hexenal, (*E*)-2-heptenal, (*E*)-2-decenal, (*E*,*E*)-2,4-heptadienal, (*E*,*E*)-2,4-decadienal, pentanoic and hexanoic acids.

Recently, Chinese-style foods flavoured with deep-fried shallot flavouring are becoming increasingly popular. Conventionally, however, the deep-fried shallot flavouring was primarily prepared with soybean oil as soybean oil-shallot flavouring. Oxidation of lipid such as soybean oil, with high contents of polyunsaturated fatty acids during deep-frying may produce oxygen radicals and harmful free radicals (Halliwell & Gutteridge, 1984), Thus, the demand for fats or oils, with low or no polyunsaturated fatty acid contents, as the frying oil has now increased.

Other fats or oils selected for substitution of soybean oil were lard, corn oil and medium-chain triglyceride

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(MCT). Lard is traditionally used in Chinese cooking and favoured by Chinese people due to its unique aroma. MCT that consists merely of octanoic and decenoic acids (Megremis, 1991), is odourless and shelf stable, and commonly used as a solvent for essential oils. Corn oil has a profile of fatty acid composition similar to that of soybean oil, except for its linolenic acid content (Peterson & Johnson, 1978). However, the flavour profile of deep-fried shallot flavourings prepared with fats or oils, other than soybean oil, is unknown. Therefore, our objective was to investigate and evaluate the volatile compounds of deep-fried shallot flavourings prepared with various oils, including soybean and corn oils, lard and MCT.

2. Materials and methods

2.1. Materials

Shallots were purchased at a local market in Taichung, Taiwan. Soybean and corn oils, lard, and MCT were commercially obtained from a local market and used as the frying oils.

2.2. Sample preparation

Peeled shallots were cut into slices of approximately 2-mm thickness using a slicer. Shallot slices (30 g) were put into a pot containing 100 g of frying oil (soybean, corn oils, lard or MCT) and then deep-fried at 150–160°C. After 5 min of deep-frying, the colour of shallots changed to dark brown. The mixture of deep-fried shallot slices and oil, also called deep-fried shallot flavouring, was immediately cooled to room temperature using an ice-water bath and used as a sample. Three samples were prepared as described for each oil used.

2.3. Flavour isolation

The mixture of deep-fried shallots and oil (130 g), with the ratio of shallots to oil of 1:3.3, was put into a modified Likens-Nickerson apparatus. After 2 ml of the internal standard [propyl propionate (Aldrich, Milwaukee, WI), 53 mg in 50 ml diethyl ether/*n*-pentane, 1:1, v/v] was added, the deep-fried shallot flavouring was immediately subjected to the flavour isolation. A mixture of 25 ml diethyl ether (Merck, Darmstadt, Germany, glass distilled) and 25 ml *n*-pentane (Merck, glass distilled) was used as an extractant. The simultaneous steam distillation-solvent extraction was allowed to proceed for 2 h, and the extract thus obtained was dried over anhydrous sodium sulphate (Merck) and filtered. The filtrate was preconcentrated at 40°C in a distillation apparatus packed with glass beads and then carefully reconcentrated to approximately 50 µl using a 10 cm×0.2 mm i.d. Vigreux column (Tung Kawn Glass Co., Hsinchu, Taiwan) at 40°C.

2.4. Gas chromatography–mass spectrometry

A Hewlett-Packard 5890A Series II gas chromatograph, coupled to a HP 5972A MSD mass spectrometer, was used. A 60 m×0.32 mm fused silica WCOT capillary column, coated with DB-Wax (0.25 µm film thickness, J&W Scientific, Folsom, CA), was used and interfaced directly into the ion source of a mass spectrometer. The operating conditions were the same as described in Chyau, Lin and Mau (1997). Retention indices of the volatile components were calculated with *n*-paraffins (C_5–C_{25}) as references (Schomberg & Dielmann, 1973). Volatile components were identified by comparing the mass spectral data with spectra available from the Wiley/NBS mass spectral library (Hewlett-Packard, Palo Alto, CA). Some compounds were further identified using authentic compounds. The amount of each component was determined using an internal standard method (propyl propionate as the internal standard) and calculated by each peak area of the ion spectrum.

3. Results and discussion

Deep-fried shallot flavourings, prepared with soybean, corn oils, lard and MCT were referred to as soybean oil-, corn oil-, lard- and MCT-shallot flavourings, respectively. Fig. 1 shows the total ion chromatogram of volatile compounds of freshly prepared deep-fried shallot flavourings. Totally, 30 compounds were identified by comparing their retention indices and mass spectral data with previously reported data (Block, Putman, & Zhao, 1992; Chan, et al. 1991; Chen & Wu, 1982; Chou, Liou & Wu, 1983; Chyau, et al. 1997; Wu & Wu, 1981; 1982; Wu et al. 1982), and those from the Wiley computer library (Table 1). In addition, 16 compounds were further confirmed by authentic compounds. This study identified fewer sulphur-containing compounds than those found by Chan et al. (1991). Furthermore, compared to a similar deep-fried soybean oil-shallot flavouring, which was prepared at the same temperature for a shorter time of 3 min (Chyau et al. 1997), this study identified fewer pyrazine compounds but more lipid-degraded compounds such as (*E*)-2-hexenal and (*E*)-2-heptenal.

Soybean oil-, lard- and corn oil-shallot flavourings contained 28 compounds, whereas only 17 compounds were found in MCT-shallot flavouring. The total amounts of volatiles were in the order of 70.2, 56.8, 43.6 and 23.3 mg kg^{-1} for lard-, corn oil-, MCT- and soybean oil-shallot flavourings, respectively. In the four flavourings, 2,5- and 2,6-dimethylpyrazines were found

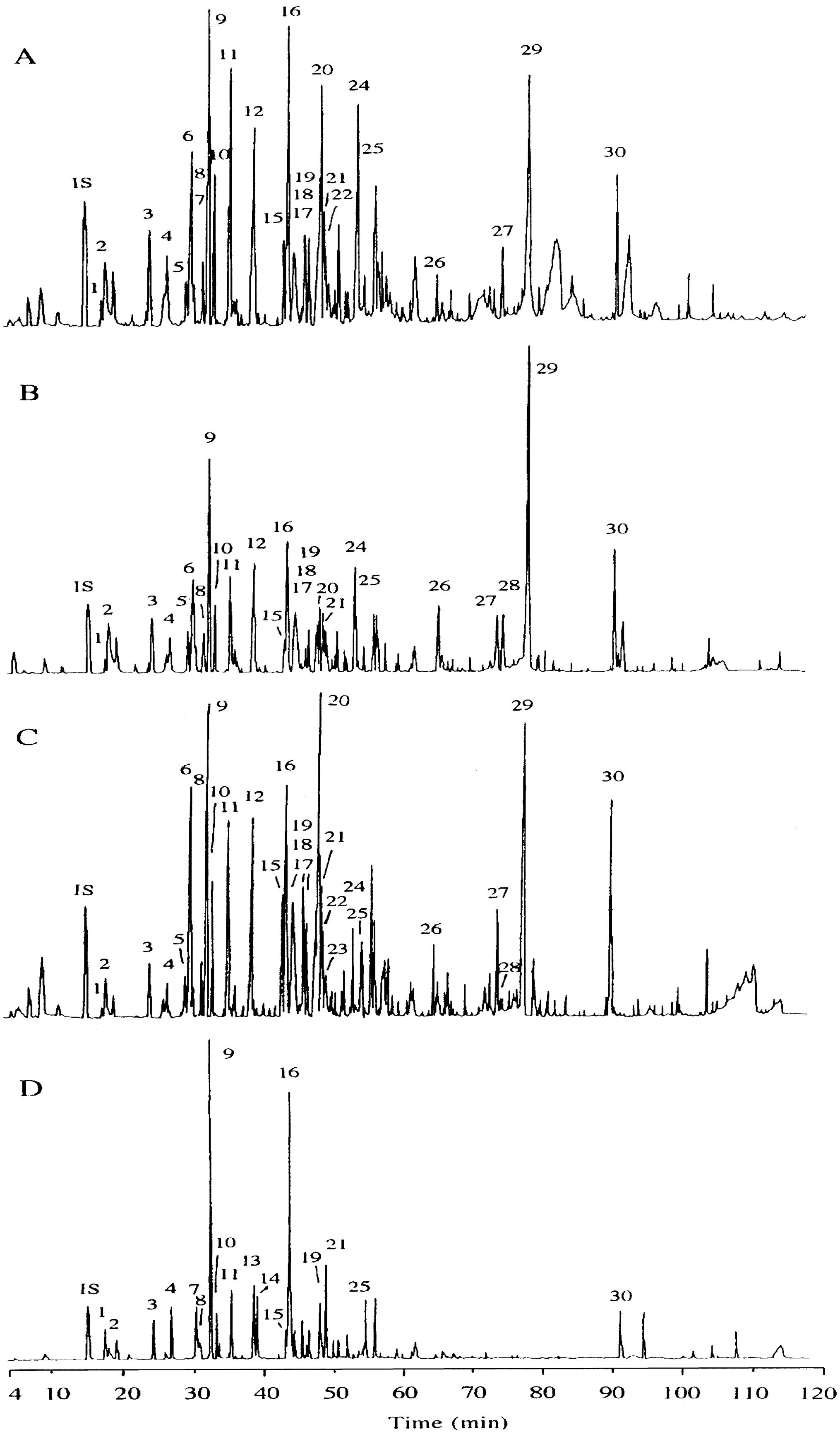

Fig. 1. Total ion chromatograms of deep-fried shallot flavourings prepared with various oils. A, soybean oil; B, lard; C, corn oil; and D, medium-chain triglycerides.

only in the MCT-shallot flavouring, and were absent in those prepared with the other edible oils. However, 13 oxygen-containing compounds, which resulted from the thermal degradation of normal edible oils, were not found in the MCT-shallot flavouring.

Volatile compounds of deep-fried shallot flavouring were compiled into three classes, including nitrogen-, oxygen- and sulphur-containing compounds, based on the heteroatom included therein(Fig. 2). The amounts of nitrogen-containing compounds were at two levels: high in MCT-shallot flavouring, and low in shallot flavourings with the other three edible oils. The amounts of oxygen-containing compounds were in the order: lard-, corn oil-, soybean oil- and MCT-shallot flavourings. The amounts of sulphur-containing compounds were high in MCT-, and moderate in lard- and corn oil-, and low in soybean oil-shallot flavourings. Sulphur- and nitrogen-containing compounds, such as sulphides and pyrazines, which were the characteristic flavours of deep-fried shallot flavourings, were remarkably high in MCT-shallot flavouring. Accordingly, MCT-shallot flavouring with more characteristic flavour might be the flavouring of choice.

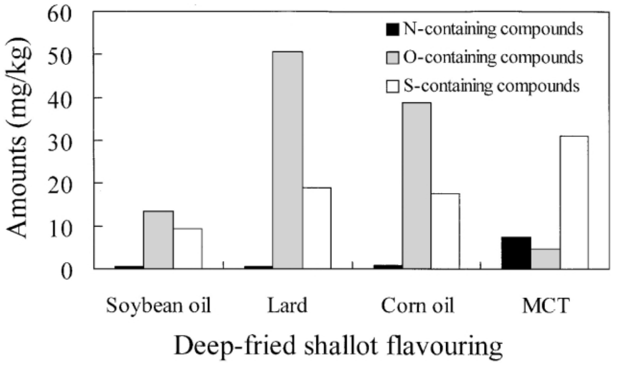

Fig. 2. Chemical classes of volatile compounds from deep-fried shallot flavourings prepared with various oils. MCT, medium-chain triglycerides.

Table 1
Volatile compounds of deep-fried shallot flavourings prepared with various oils

Peak No.[a] compound	RI[b]	Amounts (mg kg^{-1})[c]			
		A	B	C	D
1 Dimethyl disulphide[d]	1083	0.18±0.09	0.21±0.17	0.09±0.03	0.67±0.07
2 Hexanal[d]	1090	0.57±0.30	0.84±0.47	0.75±0.08	0.21±0.09
3 2-Methyl-2-pentenal	1167	0.66±0.31	0.75±0.37	0.46±0.15	1.04±0.26
4 2,5-Dimethyl thiophene	1202	0.50±0.46	0.38±0.26	0.15±0.10	1.33±0.40
5 (*E*)-2-Hexenal[d]	1236	0.26±0.16	0.60±0.07	0.93±0.84	nd[e]
6 2-Pentylfuran[d]	1240	1.43±0.64	4.11±2.76	3.23±1.43	nd
7 Methyl propyl disulphide[d]	1243	0.34±0.06	0.62±0.53	0.35±0.24	1.96±1.00
8 1-Pentanol[d]	1259	0.36±0.18	0.81±0.30	0.84±0.40	1.41±1.25
9 2,4-Dimethylthiophene	1264	2.05±0.87	4.09±3.15	2.23±1.10	10.22±5.86
10 (*Z*)-Propenyl methyl disulphide	1273	0.79±0.37	1.47±1.02	1.07±0.60	1.53±1.18
11 (*E*)-Propenyl methyl disulphide	1297	1.61±0.73	3.28±2.23	2.41±1.54	3.61±3.15
12 (*E*)-2-Heptenal	1332	1.83±0.81	4.55±2.45	3.90±2.68	nd
13 2,5-Dimethylpyrazine[d]	1335	nd	nd	nd	1.76±0.34
14 2,6-Dimethylpyrazine[d]	1341	nd	nd	nd	1.32±0.36
15 Dipropyl disulphide[d]	1390	0.47±0.34	1.20±0.79	2.36±2.42	0.51±0.28
16 Dimethyl trisulphide[d]	1392	2.14±0.73	4.58±3.24	3.62±3.35	8.46±5.36
17 Nonanal[d]	1397	0.66±0.40	5.88±3.93	4.98±4.01	nd
18 (*E*)-2-Octenal	1430	0.41±0.30	2.64±1.87	1.71±1.15	nd
19 (*E*)-Propenyl propyl disulphide	1447	1.17±0.75	3.17±2.14	5.29±5.06	2.76±2.47
20 1-Octen-3-ol[d]	1454	0.56±0.42	2.03±1.32	1.71±1.31	nd
21 2-Ethyl-3,6-dimethylpyrazine[d]	1459	0.30±0.10	0.33±0.10	0.29±0.11	3.14±1.94
22 1-Heptanol	1462	0.05±0.02	1.03±0.93	0.32±0.12	nd
23 (*E*,*Z*)-2,4-Heptadienal	1471	0.39±0.32	1.02±0.57	0.15±0.03	nd
24 (*E*,*E*)-2,4-Heptadienal[d]	1508	1.57±0.97	3.88±2.24	0.74±0.37	nd
25 2,5-Dimethyl-3-propylpyrazine	1525	0.34±0.26	0.24±0.09	0.58±0.28	1.13±0.34
26 (*E*)-2-Decenal	1645	1.38±0.60	3.43±2.61	1.24±1.21	nd
27 (*E*)-2-Undecenal	1754	0.03±0.01	2.95±2.49	2.40±1.99	nd
28 (*E*,*Z*)-2,4-Decadienal[d]	1767	0.31±0.18	2.29±1.28	4.55±0.43	nd
29 (*E*,*E*)-2,4-Decadienal[d]	1815	2.05±1.76	12.3±8.09	9.06±7.80	nd
30 2-Hexyl-5-methyl-2(5*H*)-furan-3-one	1999	0.89±0.23	1.55±0.25	1.95±0.28	1.96±1.87
Total		23.3±12.31	70.2±45.71	56.8±38.84	43.6±26.49

[a] The peak numbers correspond to Fig. 1.

[b] RI, retention indices, using *n*-paraffin (C_5-C_{25}) as references.

[c] Deep-fried shallot flavouring prepared with: A, soybean oil; B, lard; C, corn oil; and D, medium-chain triglycerides (triplicate experiments).

[d] Mass spectrum and retention index are consistent with those of authentic compounds.

[e] nd, Not detected.

Among the oxygen-containing compounds, carbonyl compounds were alleged to be produced from the thermal decomposition of lipid during the deep-frying process and have been found in the volatiles of deep-fried soybean oil (Wu & Chen, 1992). Other compounds among the oxygen-containing compounds were products from the pyrolysis of carbohydrates, such as 2-pentylfuran and 2-hexyl-5-methyl-2(5*H*)-furan-3-one. These compounds are mainly found in smoked foods (Hollenbeck, 1994) and, thus, they might contribute a slightly smoky flavour to deep-fried shallot flavourings.

Although shallots and garlic belong to the same genus *Allium*, sulphur-containing compounds in shallot flavourings, which contained the propenyl group in their structures, differed substantially from sulphur-containing compounds in garlic, which contained the allyl group (Jirovetz, Jager, Koch & Remberg, 1992; Mazza, Ciaravolo, Chiricosta & Celli, 1992). However, these sulphur-containing compounds were similar to those in onions (Boelens, de Valois, Wobben & van der Gen, 1971). Nitrogen-containing compounds such as alkyl pyrazines, have been recognized as contributing to the characteristic flavours of a large number of cooked, roasted, toasted and deep-fried foods (Maga, 1982). It is known that nitrogen-containing compounds are primarily formed from the reaction of nitrogenous substances degraded from amino acids, peptides and proteins with carbohydrate-degraded components (Shibamoto, 1980). 2-Ethyl-3,6-dimethylpyrazine was high in MCT-shallot flavouring (3.14 mg kg^{-1}) as compared to other shallot flavourings (0.29–0.33 mg kg^{-1}). This compound has a flavour threshold of 0.4 parts in 10^9 parts of water (Guadagni, Buttery & Turnbaugh, 1972) and thus, may contribute significantly to the flavour of deep-fried shallot flavourings, more especially the MCT-shallot flavouring.

Hexanal and (*E*,*E*)- and (*E*,*Z*)-2,4-decadienals were the major lipid-degraded compounds formed in the volatiles of shallot flavourings (Chen & Wu, 1982; Wu et al. 1982), and reported as the primary oxidation products of linoleic acid (Ho et al. 1989). Due to its extremely low odour threshold (0.07 μg kg^{-1}), 2,4-decadienal should be a significant oily odorant for shallot flavourings. However, MCT-shallot flavouring was devoid of any noticeable oily note.

With regard to the profile of volatile compounds, MCT-shallot flavouring was evidently different from the shallot flavouring prepared with the other three edible oils. This discrepancy in the volatile profile was mainly due to the fact that MCT consisted merely of saturated eight- and ten-carbon fatty acids (Megremis, 1991). As a result of this, MCT-shallot flavouring was low in oxygen-containing compounds and gave rise to an aroma with a much less oily note. In contrast, more unsaturated long-chain fatty acids present in the other three edible oils resulted in wide varieties of degraded compounds during deep-frying. Among these, the volatile compounds in lard-shallot flavouring were predominantly oxygen-containing compounds, resulting in a more oily note. Lard contained 47.0% saturated fatty acids, 43.0% oleic and 10.0% linoleic acids (Peterson & Johnson, 1978). Presumably, its high oleic acid content might contribute to this oily note.

Soybean oil- and corn oil-shallot flavourings were similar in their profiles of volatile compounds but varied in total amounts. However, corn oil-shallot flavouring contained more oxygen- and sulphur-containing compounds, and thereby, gave rise to an aroma characteristic of shiitake. Soybean oil contained 15.2% saturated fatty acids, 22.3% oleic, 54.5% linoleic and 8.0% linolenic acids, whereas corn oil contained 14.7% saturated fatty acids, 26.6% oleic and 58.7% linoleic acids (Peterson & Johnson, 1978). Apparently, soybean and corn oils had similar fatty acid profiles, except for the linolenic acid content. Corn oil contained no linolenic acid; therefore, after deep-frying, no thermal degradation products resulted from linolenic acid. This might be the main reason for differences in their profiles of volatile compounds.

MCT-shallot flavouring exhibited a much lighter aroma due to a smaller content of oxygen-containing compounds and hence, a much less rancid note. In addition, MCT-shallot flavouring contained high amounts of nitrogen- and sulphur-containing compounds, giving a typical shallot flavour. Therefore, the use of MCT as a frying oil may provide a shallot flavouring with better acceptability. To study the application of MCT-shallot flavouring in Chinese cuisine, further research in sensory evaluation is in progress.

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