Analysis of Cooking Oil Fumes by Ultraviolet Spectrometry and Gas Chromatography−Mass Spectrometry

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This paper investigated the components, especially aldehydes, in the fume condensates from four kinds of cooking oil using ultraviolet (UV) spectrometry and gas chromatography−mass spectrometry (GC-MS). It was observed that there was a great change of the UV absorption spectra from the results of the unheated oil to the results of the fume after heat treatment (190−200, 230−240, and 270−280 °C). There was a strong peak within the wavelength range of 260−270 nm in each condensate sample. From the GC-MS results, it was tentatively deduced that there were some 2,4-dialkylenaldehydes and other conjugated compounds in the condensates. The results showed there were large amounts of hexanal and 2-heptenal in the cooking oil fume and that the total aldehyde peak areas of the condensates from four kinds of oil were around 30−50% of the total peak area at 270−280 °C.

Keywords: *Cooking oil fumes; ultraviolet spectrometry; gas chromatography−mass spectrometry; aldehydes*

INTRODUCTION

Stir frying, frying, and deep frying are three types of traditional Chinese cooking methods involving frying food in oil. The Chinese people have the cooking habit of waiting for fumes to emit from cooking oils before they begin to cook. Epidemiological data have indicated that cooking oil fumes may be mutagenic and carcinogenic, and a positive relationship was observed between exposure to cooking oil fumes and lung cancer (*1*−*5*). Qu et al. (*6*) also reported that vapors from rapeseed oil were mutagenic. Many studies have suggested that there were large amounts of aldehydes from the headspace of cooking oil and food. Yasuhara and Shibamoto (*7*) studied the aldehydes and ketones in the headspace of heated pork fat and stated that the major compounds produced were hexanal, heptanal, and pentanal. Yasuhara (*8*) analyzed the vapors from corn oil, cottonseed oil, and soybean oil and identified 11 aldehydes. Yasuhara et al. (*9*) found that the largest quantities of aldehydes formed from various kinds of fish flesh during heat treatment were formaldehyde and acetaldehyde. Chung et al. (*10*) identified 22 aldehydes in headspace samples of peanut oil undergoing thermal treatment. Umano et al. (*11*, *12*) identified 18 aldehydes and acrolein from overheated beef fat and heated cooking oil. Wu et al. (*13*) reported that there was a significant amount of aldehydes from heated edible oils during storage. Takeoka et al. (*14*) found that there was a high amount of aldehydes in used frying oils. Snyder (*15*) determined 19 aldehydes from the headspace of soybean oil and sunflower oil stored at 60 °C for 8 days. Mussinan and Walradt (*16*) isolated 25 aldehydes from the volatile constituents of pressure-cooked pork liver.

To our knowledge, there have been no reports of the study of the differences in the composition of fume condensates from different kinds of oils heated under three different ranges of temperatures. In this paper, we used ultraviolet (UV) spectrometry and gas chromatography−mass spectrometry (GC-MS) to study the components, especially aldehydes, of the fume condensates from four kinds of cooking oils heated at three temperature ranges (190−200, 230−240, and 270−280 °C).

EXPERIMENTAL PROCEDURES

Materials. Soybean salad oil, rapeseed oil, and rapeseed salad oil were purchased from a local supermarket. Lard was refined from pork fat.

Collection of Cooking Oil Fume Condensate. One hundred milliliters of oil (lard, 100 g) was placed in a 500 mL three-neck round-bottom flask. The flask was connected to a distilling head, an air pipe, and a thermometer, respectively. The distilling head was connected to a water condenser. The receptor Erlenmeyer flask was immersed into a saltwater−ice bath. Air was piped into the round flask at a mild and stable flow with an air pump. The oil was heated to a certain temperature range (190−200, 230−240, or 270−280 °C) using a thermostatic regulator. Heating continued for another 2 h after the required temperature was reached.

Samples of 0.02 mL of the oils and the condensates were taken from the Erlenmeyer flask, placed into a 10 mL volumetric flask, dissolved with petroleum ether (60−90 °C), diluted to the mark line, and kept at 4 °C for the use of UV scan. Also, 0.1 mL of condensate from the same Erlenmeyer flask was diluted to 1 mL with petroleum ether (60−90 °C) and kept refrigerated until analyzed by GC-MS.

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Table 1. Relative Peak Area of Aldehydes from Condensates of Rapeseed Oil and Rapeseed Salad Oil Fumes

	peak area %					
	rapeseed oil			rapeseed salad oil		
aldehyde	190−200 °C	230−240 °C	270−280 °C	190−200 °C	230−240 °C	270−280 °C
3-methyl-2-butenal	0.32	0.76	ND[a]	0.78	0.50	0.22
hexanal	1.26	2.77	3.04	2.09	2.49	2.73
2-hexenal	0.21	0.45	0.22	0.38	0.47	0.25
heptanal	0.22	0.88	1.83	0.24	0.54	1.54
2-heptenal	2.10	3.82	3.61	3.30	4.23	4.42
2,4-heptadienal	3.08	2.26	3.42	8.11	4.58	1.19
octanal	0.34	0.82	2.00	ND	ND	1.05
2-octenal	0.39	0.88	1.05	ND	0.46	0.90
nonanal	1.24	5.03	9.58	ND	2.27	7.47
2-nonenal	0.15	0.63	1.28	ND	ND	0.72
2,4-nonandienal	ND	ND	ND	ND	0.47	0.27
decanal	0.01	0.16	0.45	ND	ND	0.28
2-decenal	1.43	5.23	7.29	ND	1.99	7.42
2,4-decadienal	2.73	4.45	2.47	ND	2.01	2.98
undecanal	ND	ND	0.22	ND	ND	ND
2-undecenal	1.34	0.20	4.05	ND	1.89	7.84
2,4-undecadienal	ND	0.08	0.29	ND	ND	0.21
dodecanal	ND	ND	0.18	ND	ND	ND
9-octadecenal	ND	ND	ND	ND	ND	0.23
9,17-octadecadienal	ND	ND	ND	ND	ND	0.30
total aldehydes peak area %	14.82	28.42	40.98	14.90	21.90	40.02

[a] ND, not detected.

Table 2. Relative Peak Area of Aldehydes from Condensates of Soybean Salad Oil Fumes and Lard Fumes

	peak are %					
	soybean salad oil			lard		
aldehyde	190−200 °C	230−240 °C	270−280 °C	190−200 °C	230−240 °C	270−280 °C
3-methyl-2-butenal	0.64	0.73	0.85	0.29	ND[a]	0.41
hexanal	7.38	6.81	7.67	7.15	8.93	17.93
2-hexenal	1.13	1.48	1.37	1.67	1.33	1.77
heptanal	0.95	0.55	0.39	0.86	1.58	5.62
2-heptenal	12.71	10.23	10.90	13.08	10.14	13.04
2,4-heptadienal	1.48	2.44	5.06	5.44	3.32	0.98
2,4-dimethylpentanal	ND	0.15	ND	ND	ND	ND
octanal	ND	ND	ND	1.04	1.21	2.62
2-octenal	0.80	0.47	0.77	1.17	0.93	0.83
nonanal	0.83	0.17	0.30	1.51	1.89	3.15
2-nonenal	ND	ND	ND	0.25	0.28	0.29
2,4-nonadienal	1.37	1.40	0.75	ND	ND	ND
decanal	ND	ND	ND	ND	ND	0.18
2-decenal	0.67	ND	ND	ND	1.81	1.27
2,4-decadienal	2.74	0.64	1.56	0.47	2.05	0.83
2-undecenal	0.64	ND	ND	0.51	1.45	0.85
9,17-octadecadienal	ND	3.48	ND	ND	ND	ND
total aldehydes peak area %	31.34	28.55	29.62	34.54	34.92	49.77

[a] ND, not detected.

Instrumental Analysis. A Beckman Du-7 UV−visible spectrometer was used to scan from 210 to 300 nm and to plot the graphs. A Hewlett-Packard (HP) model 5890 gas chromatograph combined to a JMS Aotomass MS equipped with a 30.0 m × 0.25 mm i.d. DB-5 column (J&W Scientific, Folsom, CA) was used for constituent analysis. The oven temperature was held at 40 °C for 10 min and then programmed to 220 °C at 3 °C/min and held for another 5 min. Mass spectra were obtained by electron impact ionization at 70 eV and a source temperature of 200 °C. High-purity helium (99.999%) was used as the gas carrier. Identifications were based on the comparison of known (from computer library) and unknown mass spectra. Relative peak areas of aldehydes (Tables 1 and 2) were calculated automatically using the integrator method. Mass spectral data and retention times of aldehydes are listed in Table 3.

RESULTS AND DISCUSSION

The UV scan spectra are shown in Figure 1. Compared with the UV spectra of the unheated oils, we found that there was a great change in the spectra after heat treatments (190−200, 230−240, and 270−280 °C). This was due to the large amounts of aldehydes formed from unsaturated fatty acids during heat treatment. There was a strong peak in the wavelength range of 260−270 nm when the oil was subjected to high-temperature treatment. This result suggested that there were some 3−5 conjugated double-bond compounds such as conjugated multialkyene and conjugated unsaturated aldehydes, ketones, and so on in the fume. From the GC-MS results, we tentatively deduced that there was a high concentration of 2,4-dialkylenealdehydes such as 2,4-heptadienal, 2,4-decadienal, and other conjugated double-bond compounds in the fumes.

Meanwhile, the results from the 12 graphs of condensates showed that there was an identical change pattern of absorption strength under the three temperature ranges. That is, the absorption strength rose when the oil temperature increased from 190−200 to 230−

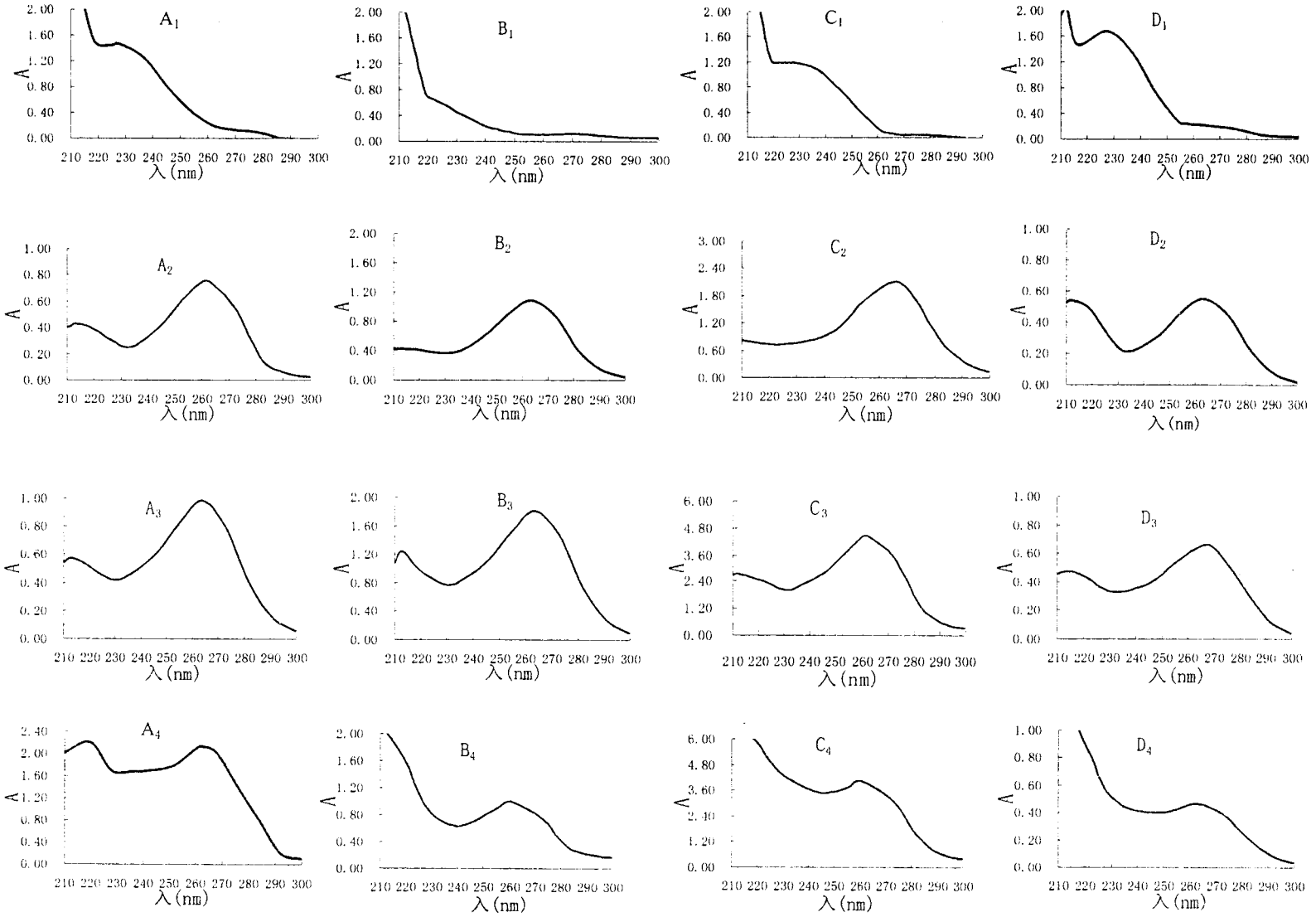

Figure 1. UV spectra of oils and their fume condensates under different temperatures: (A) soybean salad oil; (B) rapeseed oil; (C) rapeseed salad oil; (D) lard; (1) UV spectra of oils themselves; (2) UV spectra of condensates under 190−200 °C; (3) UV spectra of condensates under 230−240 °C; (4) UV spectra of condensates under 270−280 °C.

Table 3. Retention Times and Mass Spectral Data of Aldehydes

no.	aldehyde	retention time (min)	mass spectral data[a]
1	3-methyl-2-butenal	4.02	55, 41, 83, 39, ..., 69
2	hexanal	5.37	44, 56, 41, 43, 57, ..., 100
3	2-hexenal	7.80	41, 55, 69, 83, 39, ..., 98
4	2,4-dimethylpentanal	10.58	43, 58, 57, 41, 39, ..., 114
5	heptanal	11.32	43, 41, 70, 44, 55, 56, ..., 114
6	2-heptenal	15.45	41, 83, 55, 57, 56, ..., 112
7	2,4-heptadienal	18.15	81, 39, 41, 53, 67, 95, ..., 110
8	octanal	18.62	43, 41, 57, 55, 84, 69, ..., 128
9	2-octenal	22.07	41, 55, 70, 39, 83, ..., 126
10	nonanal	24.92	41, 43, 57, 56, 44, ..., 142
11	2-nonenal	27.90	41, 43, 55, 70, 83, 96, ..., 140
12	decanal	30.38	43, 41, 57, 55, 44, 70, 71, ..., 156
13	2,4-nonadienal	31.25	81, 41, 39, 53, ..., 138
14	2-decenal	33.25	41, 43, 55, 70, 39, 83, 69, ..., 154
15	undecanal	35.62	43, 41, 57, 55, 67, ..., 170
16	2,4-decadienal	35.82	81, 41, 39, 55, 67, ..., 152
17	2-undecenal	38.10	41, 70, 55, 43, 83, ..., 168
18	dodecanal	40.17	43, 57, 41, 82, 68, ..., 184
19	2,4-undecadienal	43.72	81, 41, 55, 39, ..., 166
20	9,17-octadecadienal	54.45	67, 81, 41, 54, 95, 53, ..., 264
21	9-octadecenal	58.85	55, 41, 69, 43, 67, 83, ..., 266

[a] These data were taken from the mass spectra of known compounds (computer library), and the mass spectra of the unknown compounds matched the known one.

240 °C. It can be expected that the oxidation rate of fatty acids increased with the increase in temperature and that this contributed to form conjugated compounds. However, the absorption strength decreased as the oil temperature increased from 230−240 to 270−280 °C. This occurred because some conjugated compounds were involved in secondary reactions and formed other nonconjugated products.

The absorption spectra of the four kinds of oil fume condensates indicated that the absorption strength of the rapeseed salad oil was the strongest followed by rapeseed oil, soybean salad oil, and lard. This is because of the large amount of linolenic acid (8.4%) in rapeseed oil. The autoxidation rate of linolenic acid is 77 times higher than that of oleic acid (*17*), accounting for the strongest absorption of the rapeseed salad oil fume condensate. Confirming the result with the GC-MS analysis, the total peak area of 2,4-dialkylenaldehydes in the rapeseed salad oil fume condensate was higher than that in the lard fume condensate obtained under the same condition. The total peak areas of 2,4-dialkylenaldehydes of fume condensates under 190−200, 230−240, and 270−280 °C were 8.11, 7.06, and 5.37% of total peak area for rapeseed salad oil and 5.91, 4.65, and 1.81% of total peak area for lard, respectively. The amount of 2,4-dialkylenaldehydes decreased as the temperature increased from 190−200 to 270−280 °C. This is because some unsaturated aldehydes can undergo secondary reaction and form other compounds.

It has been reported that there are large amounts of aldehydes in the headspace of cooking oils. Aldehydes are considered as possible contributors to carcinogenicity (*18*−*20*). By comparing our unknown mass spectra to library mass spectral data, we tentatively identified 21 aldehydes such as 3-methyl-2-butenal, hexanal, 2-hexenal, and heptanal. All of the aldehydes from different oils are shown in Tables 1 and 2. The total aldehyde peak area of the condensate from the four cooking oils used in this study ranged from 15 to 35% at 190−200 °C, from 22 to 35% at 230−240 °C, and from 30 to 50% at 270−280 °C, respectively.

From Table 1, we can see that the total aldehyde peak area of rapeseed oil fume condensate elevated remarkably as the temperature of the oil increased. The total peak area of aldehydes at a temperature of 270−280 °C was 3 times as much as that at the temperature of 190−200 °C. This was because the oxidation rate of lipid increased as the temperature increased. The relative peak areas of nonanal and 2-decenal increased obviously as the temperature increased from 190−200 to 230−240 and 270−280 °C, and the peak areas were 1.24, 5.03, and 9.58% and 1.43, 5.23, and 7.29%, respectively. High amounts of oleic acid (14.00%) and tetracosenic acid (47.50%) in the rapeseed oil helped to form those aldehydes. The total peak area of aldehydes from rapeseed salad oil fume condensate (Table 1) was nearly the same as that of rapeseed oil fume condensate when they were undergoing the same treatment. It was suggested that there was a similar formation mechanism of aldehydes between the rapeseed oil fume and rapeseed salad oil fume because these two oils had almost the same components except for some impurity in the rapeseed oil.

Table 2 shows that there is little change of the total aldehyde peak area in the soybean salad oil condensate under the three different temperature ranges. Soybean salad oil may contain a higher concentration of antioxidants such as vitamin E than the other three oils. On the other hand, we tentatively identified 2,4-dimethylpentanal in the soybean salad oil fume condensate, whereas none was detected in the other oil fume condensates. High levels of hexanal, 2-heptenal, and 2,4-heptadienal were formed due to the large amount of linoleic acid (51.70%) in the soybean salad oil. There was a certain linolenic acid (7.60%) in this oil, and therefore a large amount of 2,4-heptadienal was identified from the sample.

Generally, saturated fatty acids are more resistant to oxidation than unsaturated ones. Although lard contains a high level of saturated fatty acids, they can be easily oxidized to form cleavage products when subjected to temperatures of >150 °C (*13*). Table 2 shows that there is a large proportion of aldehydes formed under all three of the temperature ranges. Linoleic acid is one of the main constituents of lard. It is generally recognized that oxidative cleavage of double bonds produces aldehydes or ketones (*21*), which accounts for the result that heptenal and 2-heptenal are the major constituents of the fume condensate of heated lard. Yasuhara et al. (*7*) also found that hexanal was the major component of the headspace of heated pork fat. Another possible reason is that there are few antioxidants in the lard leading to thermal oxidation and cleavage.

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