

Relationship between oil fume mutagens in ambient air and the deterioration of heated edible oils*

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Abstract—When rapeseed oil, soybean oil and peanut oil were heated in air at the typical Chinese cooking temperature 270—280°C for 30min, their anisidine values significantly increased. The contents of C18:3 in rapeseed and soybean oils significantly decreased; in these two oil fumes the mutagen α,β -unsaturated aldehydes - crotonaldehyde and 2-methylacrolein were found respectively. Since there was no C18:3 in peanut oil, no mutagen was found in its fume. Consequently it showed that the heated rapeseed oil and soybean oil contained significant amount of α,β -unsaturated aldehydes—the decomposition products of the hydroperoxide of C18:3 which closely related to the formation of the oil fume mutagens in ambient air.

Keywords: edible oils; anisidine value; C18:3; α,β -unsaturated aldehydes; oil fume mutagens.

1 Introduction

Nowadays 90% of human's activity is carried out in indoor and therefore the quality of indoor air affects human health directly. Certain researchers (Gao, 1987) have reported the volatile lipid oxidation products from kitchen might cause lung cancer. The oil fumes produced by heating edible oils at high temperature are mutagenic and probably it is one of the main cause of indoor air pollution (Qu, 1990). The mechanism of toxicity of thermally and oxidatively derived oxygenated products has not been clarified. Edible oils belong to the triglycerides (Hilditch, 1964). During processing or in the course of storage the triglycerides of unsaturated fatty acids like oleic acid, linoleic acid and linolenic acid were easily oxidized in air forming a series of hydroperoxides by free radical autoxidation (Frankel, 1985). They are readily decomposed thermally into volatile and nonvolatile oxidation products. Metal may catalyze the autoxidation and decomposition of the hydroperoxides (Frankel, 1983). In the volatile condensates of the heated oxidized edible oils, most researchers (Frankel, 1983; 1985; Mounts, 1986; Wu, 1992; Neff, 1993) have made their contributions to the change of flavor. By separation and identification the mutagenic components - crotonaldehyde and 2-methylacrolein were found respectively in the volatile condensates of the heated rapeseed oil and soybean oil, and the mechanism of formation of crotonaldehyde has been studied (Bao, 1994). The α,β -unsaturated - aldehydes - crotonaldehyde and 2-methylacrolein have been identified to be mutagens (Lutz, 1982; Marnett, 1985).

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But the relationship between the formation of the mutagen and the deterioration of the heated edible oils are not clear. For this reason, this paper tends to prove the relationship between the quantitative measurements of the changes in values of certain tests of heated edible oils by specific methods and GC, and the formation of the constituents of pollutants in their fumes on indoor air.

2 Materials and methods

2.1 Materials

Edible oils - rapessed oil, soybean oil and peanut oil were purchased from Beijing Municipal Cereals and Oils Company.

2.2 Methods

The actual cooking condition which is typically used in Chinese cooking was simulated by heating the edible oils in an open small size iron wok at 270—280°C for 30 min, respectively. Eventually the anisidine value, carbonyl value, peroxide value and the changes in fatty acids contents such as stearic acid, oleic acid, linoleic acid, linolenic acid and erucic acid of the heated edible oils were analyzed according to the prescribed methods as follows:

Anisidine value(AV) was determined by method -2504(IUPAC,1979). Its absorbance was measured by spectrophotometer 753 (The Third Analytical Equipment Factory, Shanghai) at 350 nm.

Carbonyl value (CV) was determined by method - GB -5009, 37—85 (1988). Its absorbance was measured by spectrophotometer 753(The Third Analytical Equipment Factory, Shanghai) at 440 nm, and the carbonyl values was calculated.

Peroxide value(PV) was determined by method -2501(IUPAC,1979).

Fatty acids, oil sample was first transferred to its fatty acids methyl esters by method -2301 (IUPAC,1979) and were determined later by method -2302(IUPAC,1979). Variant gas chromatograph with SP -3700 capillary column(2m×3m ID; packed on chromosorb WAW DMCS 80—100 mesh, with 15% DEGS) was used. The column temperature was 190°C. The carrier gas is nitrogen with a flow rate of 30 ml/min. The make up gas was hydrogen with a flow rate of 30ml/min and air with a flow rate of 300ml/min. The temperature of flame ionization detector (FID) was 280°C. The rate of paper was 2.5mm/min. The size of sample was 0.6—1.0 micro-liter. The concentration of sample was 220.7—228.1mg/ml(The quantity as measured varied in different samples of methyl ester of fatty acids to be tested). The individual methyl ester was recognized by comparing the retention time with that of the standard. The quantity of each fatty acid of the sample was compared with the external standardization of the standard methyl ester of fatty acid solution in area percent and finally was calculated in weight percentage.

All reagents used were in the reagent grades. All the reagent solutions and standard solutions were prepared according to the requirements as prescribed in the above methods. All values were average from duplicate runs.

3 Results

From Table 1 we can see that the ionization value and carbonyl value increased significantly

and the large amount of α, β -unsaturated aldehydes and carbonyl compounds have formed in the heated edible oils. The peroxide values decreased in different degrees. It indicates that the hydroperoxides - the oxidative products of unsaturated fatty acids of heated edible oils decomposed during heated at high temperature.

Table 1 Changes in certain values of edible oils after heated at 270—280°C

Oils	Anisidine value, numeral	Carbonyl value, meq/kg	Peroxide value, meq/kg
Rapeseed	6.87	11.9	22.1
	82a	109.7a	21a
Soybean	6.7	9.3	27
	110.6a	143.4a	21a
Peanut	8.6	12.4	40
	72.4a	154.2a	26a

Note: a is heated edible oils

From Table 2 we can see C18:3 (linolenic acid) decreased the most, and C18:0 (stearic acid) decreased the least. It shows that the more unsaturation of fatty acids, the more decomposition. Peanut oil contains no C18:3.

Table 2 Changes in the contents of fatty acids in edible oils after heated at 270—280°C

Oils	Contents of fatty acids in weight percentage				
	C18:0	C18:1	C18:2	C18:3	C22:1
Rapeseed	1.65	15.63	15.91	9.73	36.41
	1.50a	11.84a	11.24a	5.91a	30.79a
Soybean	3.69	20.97	43.14	6.27	
	2.36a	12.76a	22.49a	2.47a	
Peanut	4.42	40.06	33.73		
	3.36a	27.06a	20.12a		

Note: a is heated edible oils

4 Discussions

Edible oils are oxidized, decomposed and hydrolyzed during processing, storage and especially heating in food cooking. Oils and fats heated at frying temperature 170—200°C contain an extremely complex mixture of products of oxidation, polymerization, hydrolysis, fragmentation and cyclization. A few information available to indicate if any of these multitude of compounds present and hazard in our modern diet (Frankel, 1985). In this experiment, polymerized resinous matter was found around the wall of the heated wok. By means of GC—MS, α, β -unsaturated aldehydes - crotonaldehyde and 2-methylacrolein as mutagen were found in the volatile condensates of heated rapeseed oil and soybean oil respectively, but none of them was found in the

volatile condensate of heated peanut oil. This agreed well to the positive results in the Ames test which were given by the extracts of the volatile condensates from rapeseed oil and refined soybean oil, but not from peanut oil respectively when they were heated at 270—280°C (Qu, 1990).

Table 1 shows that the large amounts of α, β -unsaturated aldehydes were formed in the heated rapeseed oil and soybean oil. Table 2 shows that these oils contained C18:3 and of which hydroperoxide decomposed significantly during heating. α, β -unsaturated aldehydes - crotonaldehyde and 2-methylacrolein, the mutagens were found in their fumes respectively. But peanut oil contains no C18:3 and no mutagens is found in its fume. It indicates that these mutagens are the decomposition products of C18:3 hydroperoxides. Consequently it proves that there is relationship between the deterioration of the heated rapeseed and soybean oils and the formation of the mutagens in their oil fumes on indoor air.

Aldehydes are formed from cleavage of secondary alkoxy radicals have been accepted and authenticated for the allyl system of fatty acids ester hydroperoxides (Frankel, 1983). Although the mechanism for the formation of 2-methylacrolein remains to be investigated, the mechanism for the formation of crotonaldehyde (2-butenal) can be explained to be a cleavage product from 15-hydroperoxide of 9, 12, 15-octadecatrienoic acid (linolenic acid, C18:3; Bao, 1994).

In this experiment, carbonyl compounds and hydroxyalkenals were though responsible for mutagenic compounds in the deteriorated edibles oils (Esterbauer, 1988, 1989), but they were not found in any volatile condensates, probably they were more volatile, unstable and decomposed during analysis.

According to statistics at present there are about one hundred thousand burning stoves in Shanghai streets and lanes for frying and cooking foods. The pollution of the expelled oil fumes is not inferior to that of a factory, the similar occurrences in Beijing streets and lanes and other cities all over China can be found everywhere.

Nowadays there is definite stipulation for the control of factory pollution. There is not only no law or regulation to deal with the management of the air pollution at country fair trade and streets, but also it goes so far as to pay no attention to a familiar sight. This is a widespread and serious problem. This study shows that the deterioration and the decomposition of hydroperoxide of C18:3 occur in certain heated edible oils. It not only relates to the formation of the mutagens in oil fumes but also relates to the occurrence of the pollution by the oil fumes on indoor air and ambient environment. From now on the adoption of appropriate measures and regulation for the prevention and cure of indoor and ambient air pollution, protection of the environment and people's health, this paper has highly important significance.

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