Thesis for Degree of Master of Science

*Multi Detection Methods for Analysis of Adulterated Sesame Oil (**Sesamum indicum** L.)*

by

No, Ki-Mi

Advisor Prof. Kim, Kyong-Su, Ph.D.

Department of Food and Nutrition

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A thesis submitted to the graduate faculty

in partial fulfillment of the requirement for the degree of

Master of Science

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This is to certify that the Master's thesis of

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Multi detection methods for analysis adulteration sesame oil (Sesamum indicum L.)

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This study was performed for the development of identification if added in sesame oil. Methods to identify the other vegetables oil. Sesame oil was extracted from sesame seeds originating from different countries. Adulterated sesame oil were prepared by mixing corn oil in the ratios of 0, 5, 10, 20, 30, 40, 50, 75, 80 and 100% (v/v). Soybean and rapeseed oils were also added in ratios of 0, 5, 10, 20, 40, 80 and 100% (v/v). Detection methods for adulterated sesame oil such as analysis of fatty acid by GC-FID and GC/MS, sesamin content by HPLC analysis, carbon isotope ratio and NIR spectroscopy were investigated. Also, the analysis method of volatile organic compounds by GC/MS in sesame and other vegetable oils was compared.

When sesame oil is adulterated with corn oil, adulteration ratio of corn oil more than 5% can be estimated from the ratio of $C_{16:0}\times C_{18:2}\times C_{18:3}/C_{18:0}+C_{18:1}$ fatty acids. The linear regression coefficient (r^2)

for this analysis was 0.987 and a simple equation of y=0.0072x+1.2951 was fit to the data. Soybean oil in adulterated sesame oil can be detected by the content of linoleic acid and the ratio of $C_{18:1}/C_{18:2}$ fatty acids, and rapeseed oil can be detected by the content of linoleic and erucic acid and the ratio of $C_{18:2}/C_{18:1}$ fatty acids. Linoleic acid content of more than 0.5% can be used to estimate the percent of foreign corn, soybean and rapeseed oils, and linoleic acid content of more than 1% can be used to estimate the percent of foreign soybean and rapeseed oils. Linoleic acid contents between 0.5% and 1% can be detected by carbon isotope analysis.

Analysis of sesamin content by HPLC was not applicable to the detection of adulterated sesame oil because sesame oils of different origin contain various ranges of sesamin. NIR spectroscopy was useful for discriminating the geographical origin of sesame oil but not for detection of adulterated sesame oil. Analysis of volatile organic compounds by GC/MS may be useful as a detection method for adulterated sesame oil because corn, soybean and rapeseed oils have characteristic compounds In conclusion, corn, soybean and rapeseed oil contents of more 10% (v/v) in adulterated sesame oil can be easily detected using the above methods.

INTRODUCTION

Sesame oil, a vegetable oil, is extracted from sesame seeds (*Sesamum indicum* L.) belonging to the *Pedaliaseae* family (1-7). Due to its characteristic taste and flavor, sesame oil has since ancient times been very popular in many Asian counties including Korea(8). The roasting process is an important step in making sesame oil, and the composition and quality of the oil are influenced by this process (9). Sesame oil is highly nutritious, since it contains lipid (50%), protein (20%), carbohydrate (15%), fiber (3.1%), calcium (1.2%), iron (0.0096%) and vitamins (B_1 and B_2). Sesame oil is rich in unsaturated fatty acids such as oleic acid and linoleic acid (1). It also contains a number of lipids that are natural antioxidants, such as sesamin, sesamolin, sesamol and tocopherol, and a number of unsaponifiable lipids such as oleic acid and linoleic acid.

Since the 1990s, a great deal of oil marketing have been increasing where sesame oils showing the fastest-growing by 300% from 600 million in 1993 to 1500 million in 2000. At present, the sesame oils market is still growing rapidly as several major corporations are dedicated to increase advertising and sales of sesame oil in conjunction of improving oil manufacturing facilities(10). However, sesame oil costs 15-20 times more than other vegetable oils, so it is frequently subjected to adulteration with these oils for economic reason. Although, adulterated sesame oils widely are circulated in the market they which are very difficult to estimate and identify. Consumption of the adulterated sesame oils may causes various health problems to consumers who of course

are not able to identify such oils (11). According to the Korea Consumer Protection Board, consumer inquiries related to sesame oil doubled from 22 in 1990 to 44 in 2000. 84% of the inquiries were concerned with safety and quality (12). Discernment of the adulations in oil of edible oils has been an object of concerns in many foreign countries for a long time. The Codex Alimentarius Committee on Fats and Oils of FAO/WHO announced that the scope of fatty acid composition for 17 marketed edible oils was established to distinguish edible oils.

The purity of sesame oil is assessed by a number of methods that measure acid content, iodine value, sterol content, fatty acid composition, etc., but these methods are not useful in identifying adulterated oils. Reproducible and appropriate methods for doing this are needed. There is also a need for strict management of production and marketing of adulterated sesame oils, because it destroys the usual distribution structure and creates a problem of food hygiene. Many distributors need useful and easily implemented methods for detecting adulterated sesame oil (13,14).

Many previous studies are available on the detection and identification vegetable oil contaminants in adulterated sesame oil. Lee *et al*. (15) used HPLC and the Villavecchia-suarez color reaction to determine the sesamin and sesamol contents of sesame extracts, and Hwang *et al*. (16) reported on the contents of sesamin, sesamolin and sesamin in sesame oil. Cheon *et al*. (17,18) used TLC and HPLC to investigate the triglycerol compositions of various vegetable oils. Adulteration of sesame oil has also been analyzed by spectrophotometric method (19), fatty acid and sterol compositions (20), and a combined analysis of fatty acid compositions and carbon isotope ratio (21). Recently, several studies reported that the discrimination of pure and adulterated sesame oil and the identification of the oil's origin can be carried out by NIR

analysis (22-24), and by electronic nose (25). The methods to distinguish different edible oils were developed by a computer program and graphic procedure on the based on fatty acid composition (26,27). Some studies on the geographical origin of olive oil have been carried out by pattern analysis of chemical composition (28). Detection of adulterated oils by NIR spectroscopy. Van Niekerk and Burgera noted that the presence of a foreign oil in adulterated sesame oil can be conformed by analysis of fatty acid composition and sterol and tocopherol content using a weighted least squares estimator (29). Han *et al*. (30) reported that a foreign oil in sesame oil can be detected by the peak ratio of C_{42}/C_{46} triglyceride species during HPLC. Yamazaki *et. al*. (10,31) reported that a method for identifying and estimating the mixing ratio of other vegetable oil in an adulterated sesame oil was established using the fatty acid composition of sesame oil and other vegetable oil. Many people have tried to find new methods for detection of adulterated oils, since current methods are useful only as a straightforward technique. However, current adulteration techniques require more sophisticated methods for proper identification.

This study was performed for the development of methods for the identification and multi detection of adulterated edible oils. We analyzed the general composition (fatty acid, sesamin) of sesame oils from various countries (Korea, Sudan, India, China, Pakistan). We then used multiple method and studied for multi detection methods for adulterated sesame oils, including analysis of fatty acid by GC-FID and GC/MS, sesamin content by HPLC analysis, carbon isotope ratio and near-infrared (NIR) spectroscopy. The results from these tests were compared to new method of analyzing volatile organic components by GC/MS.

MATERIALS AND METHODS

A. Materials and Reagents

1. Materials

The sesame seeds with white coat produced in Korea, Sudan, India, China and Pakistan were obtained though the Agricultural and Fishery Marketing Corporation, Korea. Sesame oil of each sample was extracted in laboratory. The other vegetable oils such as corn oils, soybean oil and rapeseed oil were purchased from local market and used for adulteration test. This sesame seeds were kept in cold room before and during analysis.

2. Reagents

The reagents used in the experiments were analytical grade and obtained from Sigma (St. Louis, MO, USA), Supelco (18918-1AMP, USA) and Fisher Scientific (Normschliff, Geratebau, USA). The standard of sesamin and the standard of triundecanoin and undecanoic acid methyl ester for analysis of fatty acid were purchased from Sigma (St. Louis, MO, USA). Fatty acid standards ($C_{8:0}$, $C_{10:0}$, $C_{11:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:2}$, $C_{18:3}$, $C_{20:0}$, $C_{22:0}$, $C_{22:1}$) were purchased from Supelco (18918-1AMP, USA). HPLC grade solvents (methanol, n-hexane n-pentane and diethyl ether) used for methyl esterification of fatty acid and extraction and chromatography were redistilled using a spiral packed double distilling apparatus (Normschliff Geratebau,

Wertheim, Germany) and Milli-Q water that was generated with a water purification system (Millepore Core Corporation, Bedford, USA). The florisil (60~100 mesh) was purchased form Fisher Scientific (Pittsburg, USA), and used to deactivating.

B. Methods

1. Mixing of sesame oil and adulterated sesame oil

Sudan, India, China, Pakistan and Korea sesame seeds were washed, dried at room temperature and roasted at 200±5℃ for 20 min with an electron heating pan. Sesame oil was extracted by method of heating and compressing with an oil presser machine (NEH-404K, National Engineering Co.) in laboratory.

The Indian sesame oil was adulterated by mixing ratios of corn oil 0, 5, 10, 20, 30, 40, 50, 75, 80 and 100% (v/v), and soybean and rapeseed oil were 0, 5, 10, 20, 40, 80 and 100% (v/v), respectively. This sesame oil was kept in cold room before and during analysis.

2. Analysis of fatty acid in sesame oil and adulterated sesame oil

a. Mixing of sample for analysis of fatty acid

AOAC official method was modified For the preparation of FAME analysis (32). 25 mg of the oil sample was taken into the test tube and 1 mL of internal standard (triundecanoin, 1000 μg/mL) and 1.5 mL of 0.5 N NaOH/methanol was added for

the saponification, and flushed with N_2 and vigorously vortexed. The sample was then heated at 100℃ water bath for 5 min, added 2 mL of 14% BF_3-methanol after cooling, flushed with N_2, vigorously vortexed and heated at 100℃ water bath for 20 min. It was cooled to 30~40℃ and added 1 mL of n-hexane, flushed with N_2, vigorously vortexed for 30 sec, added 5 mL of saturated NaCl solution and flushed with N_2 and vigorously vortexed. It was cooled to room temperature and then an aliquot of the supernatant hexane layer was transferred into an amber vial and flushed with N_2. GC analysis was carried out using this sample.

b. Analysis of fatty acid by GC

To analyze fatty acid by GC, Hewlett-Packard 5890 II Plus (Hewlett Packard, USA) attached to FID (flame ionization detector) was used. The oven temperature programmed at 100 ℃ (Isothermal for 1 minutes) was ramped to 200 ℃ at 25 ℃ /min (Isothermal for 25 minutes). The temperatures of injector and detector were 250 ℃ and 260 ℃ respectively. The capillary column used was a DB-WAX (30 m × 0.32 mm i.d., 0.25 μm film thickness, J&W, USA). Helium was used as the carrier gas at a flow rate of 1 mL/min, with as injector volume of 1 μL using 1:20 split ratio (Table 1).

c. Analysis of fatty acid by GC/MS

The GC/MS analyses of fatty acid carried out on a Finnigan Polaris Q (Finnigan, USA), in electron impact ionization (EI) mode, employing a DB-WAX (30 m × 0.32 mm i.d., 0.25 μm film thickness, J&W, USA). The GC/MS conditions used for identification of fatty acid was given in Table 2. The ionization voltage was set at 70 eV, and the injector and ion source temperatures were kept at 260℃. The other conditions were the same as for analysis method of the GC. Mass spectra were identified with the aid of our own mass spectral data and those contained within the WILEY 139, NIST 62 and NIST 12 libraries and mass spectral data books as well as by the comparison of retention indices to reference data. The results were expressed as relative percent of identified fatty acids on a molar bases, using undecanoic acid (11:0) as an internal standard.

Table 1. GC conditions for identification of fatty acid methyl ester

GC	Hewlett - Packard 5890 II Plus
Column	DB-WAX (J&W, 60 m × 0.25 ㎜ i.d., 0.25 ㎛ film thickness)
Detector	FID
Carrier gas	Helium (1.0 mL/min)
Make up gas	N_2 (30 mL/min)
Temp. program	100℃(1min)-25℃/min-200℃(25 min)
Detector temp.	260℃
Injector temp.	250℃
Split ratio	1:20 (1:50)
Injection volume	1 μL

Table 2. GC/MS Conditions for identification of fatty acid methyl ester

GC/MS	Finnigan Polaris Q
Column	DB-WAX (J&W, 60 m × 0.25 mm i.d., 0.25 μm film thickness)
Carrier gas	Helium (1.0 mL /min)
Temp. program	100℃(1 min)-25℃/min-200℃(10)-2℃/min-220℃(20 min)
Injector	250℃, split ratio 1:20
Temperature	ion source and transfer line 260℃
Ionization	electron impact ionization (EI)
Ionization voltage	70 eV
Mass range (m/z)	41 ~ 450
Injection volume	1 μL

3. Analysis of sesamin content in sesame oil and adulterated sesame oil

Sesamin, one of the main antioxidants contained in sesame oil was analysed with a HPLC (Surveyor, ThermoFinnigan, San Jose, USA). 40 g of oil was dissolved with hexane at 10 ml mass flask and 10 μL sample was used for injection(Table 3). Reversed phase separation was performed with a μ-Porasil (Waters, 10 μm, 3.9 mm × 300 mm) column. The chromatograph was operated with a mobile phase of 0.6% isopropyl alcohol in n-hexane at a flow rate 1 ml/min. The amount of each compound present was determined by the peak height at 200-600 nm with a UV detector. Peak identification was carried out by comparison of relative retention times with standard sample, and calculated from responses of peak area using a standard curve prepared by HPLC chromatography of known amount of sesamin.

Table 3. Operating conditions of the HPLC apparatus used in the study of sesamin

Instrument	HPLC(Surveyor, ThermoFinnigan, USA)
Column	μ-Porasil(Waters, 10 ㎛, 3.9 mm × 300 mm)
Wavelength	285 nm
Mobile phase	0.6% Isopropanol/in hexane
Flow rate	1.0 mL/min
Injection volume	10 μL

4. Analysis of carbon isotope ratio in sesame oil and adulterated sesame oil

The analyses of the carbon in the samples were performed using a IR/MS (ISOCHROM-EA). Samples were mixed and 0.15 mg of sample oil take in thin capsule. For carbon isotopic analyses, separated compounds were converted to CO_2 by passing the eluting analyte stream through a ceramic oxidation reactor at a temperature of 1,030℃ gas. CO_2 gas standards were injected before and after the species of interest to permit the calculation of $\delta^{13}C$ values. Helium was used as carrier gas. They are expressed in the usual permil notation relative to the Pee Dee Belemnite (PDB) marine carbonate standard.

$$\delta^{13}C\text{sample}(‰) = \left[\frac{(^{13}C/^{12}C)\text{sample}}{(^{13}C/^{12}C)\text{PDB}} - 1\right] \times 1{,}000$$

5. Analysis of NIR in sesame oil and adulterated sesame oil

The NIR spectrophotometer (U-4100 UV-Visible-NIR spectrophotometer, Hitachi, Japan) was used with the reflectance unit fitted. Measuring cell using the 10 mm cell (QS10, Hellma, Germany) scanning was carried out at an ambient temperature and over the 400~2500 nm range at 32 revolutions per scan, giving 1050 data points for each spectrum. Measured NIR spectrum differentiated original spectrum to decrease effects of dispersion by physical character in absorption values.

6. Analysis of volatile organic components of sesame oil and adulterated sesame oil

a. Extraction and concentration of volatile organic components

100 g sample was mixed with 1 L distilled water and l μL n-butyl benzene was added as an internal standard. The volatiles organic components were extracted for 2 hours with 200 mL redistilled n-pentane/diethyl ether (1:1, v/v) mixture using a simultaneous steam distillation and extraction (SDE, Likens & Nickerson type) apparatus as modified by Schultz *et. al.* (33,34) under atmospheric pressure. The extract was dehydrated for 12 hours over anhydrous sodium sulfate and concentrated to final volume approximately 0.5 mL using a Vigreux column. This sample was finally used for the GC/MS analysis.

b. Analysis of volatile organic components

(1) Establishment of retention index

Kovats (35) suggested RI (retention index or Kovats index) as suitable indication rule for retention indication which was indicated by a same compound to retention time for standard alkane.

Retention index as parameter used for checking of a solute from chromatogram by comparing the retention time of alkane that appeared the above and below of the solute.

$$RI_i = 100\ Z + 100\ \{ \frac{Log\ V_{R(i)} - Log\ V_{R(Z)}}{Log\ V_{R(Z+1)} - Log\ V_{R(Z)}} \}$$

RI_i : Retention index of compound i

$V_{R(i)}$, $V_{R(Z)}$, $V_{R(Z+1)}$: Each space revision time of alkane of compound I, carbon each number Z, Z+1

According to definition, retention time of alkane has the value as multiply of carbon number that the compound has to be unrelated with column solid phase, with temperature of separation. Therefore, n-alkane was indicated as standard index for CH_4 (RI=100), C_2H_6 (RI=200) ⋯ C_nH_{2n+2} (RI=100n), and even anything in analysis column (36).

For retention index, the dilution mixture of n-alkane; I (C_7～C_{17}) and II (C_{13} ～ C_{23}), was used as internal standard. 1μL mixture was injected to find out the retention time of internal standard by GC-FID under the condition of Table 1. RI of each peak was established by a basic program that substituted the RT of each peak of n-alkane confirmed at GC chromatogram.

(2) Analysis of volatile organic components by GC

GC conditions for analysis of volatile organic components was appeared Table 4. GC for analysis of volatile organic components was used to Hewlett-Packard 5890 II Plus (Hewlett Packard, USA) attached to FID (flame ionization detector). To volatile organic components GC was used

Hewlett-Packard 5890 II Plus (Hewlett Packard, USA) attached to FID (flame ionization detector). The temperatures of injector and detector were 250 ℃ and 300 ℃ respectively. The capillary column used was a DB-WAX (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W, USA). Helium was used as the carrier gas at a flow rate of 1mL/min, with as injector volume of 1μL using 1:20 split ratio.

(3) Analysis and identification of volatile organic components by GC/MS

The GC/MS analyses were carried out on a Shimadzu GC/MS QP-5000), in electron impact ionization (EI) mode, employing a DB-WAX (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W, USA). GC/MS conditions used for identification of volatile organic components are shown in Table 5. The ionization voltage was set at 70 eV, and the injector and ion source temperatures were kept at 250℃ and 230 ℃ respectively. The other conditions were the same as for analysis method of the GC. Helium was used as the carrier gas at a flow rate of 1.0 mL/min with an injector volume of 1 μL using a 1:20 split ratio. Mass spectra of detected compounds were identified with the aid of our own mass spectral data and those contained within the WILEY 139, NIST 62 and NIST 12 libraries and mass spectral data books (37,38) as well as by the comparison of retention indices to reference data (39,40). The results were expressed as relative percent of identified volatile organic compounds on a molar bases, using n-butylbenzene as an internal standard.

$$\text{Component Content (mg/kg)} = \frac{C\% \times 1000\ g}{A\% \times B\ g}$$

A% : Peak area of each sample of internal standard

B g : Amount of sample

C% : Peak area of each component in sample

Table 4. GC conditions for analysis of volatile components

GC	Hewlett - Packard 5890 II Plus
Column	DB-WAX (J&W, 60 m × 0.25 ㎜ i.d., 0.25 ㎛ film thickness)
Detector	FID
Carrier gas	Helium (1.0 ㎖/min)
Make up gas	N_2 (30 ㎖/min)
Temp. program	40℃(3min)-2℃/min-150℃-4℃/min-220℃(5 min)
Detector temp.	300℃
Injector temp.	250℃
Split ratio	1:20
Injection volume	1 ㎕

Table 5. GC/MS conditions for identification of volatile components

GC/MS	Shimadzu GC/MS QP-5000
Column	DB-WAX (J&W, 60 m × 0.25 mm i.d., 0.25 μm film thickness)
Carrier gas	Helium (1.0 mL/min)
Temp. program	40℃(3 min)-2℃/min-150℃-4℃/min-220℃(5 min)
Injector	250℃, split ratio 1:20
Temperature	ion source and interface 230℃
Ionization	electron impact ionization (EI)
Ionization voltage	70 eV
Mass range (m/z)	41 ~ 450
Injection volume	1 μL

RESULTS AND DISCUSSION

A. Analysis of general composition of sesame oil

Sesame oil was extracted from sesame seeds originated from different countries such as (India, Sudan, Pakistan, China) and Korea. The yield of oil expression was 53.2±1.25%. These sesame oils were used for analysis of fatty acid and sesamin content.

1. Analysis of fatty acid composition

A mixture of fatty acid methyl ester standards was analyzed by GC (Fig. 1). The retention time of each peak from the standard and the sample was compared(Table 6). The fatty acids methyl ester from different countries of origin are shown in Fig. 2. The relative composition of fatty acids in these samples is shown in Table 7.

The major fatty acids contained in sesame oil were linoleic acid (44.19±2.86%), oleic acid (39.16±2.02%), palmitic acid(10.29±0.78%), and stearic acid(5.39±0.71%), with smaller amounts of linolenic acid (0.38±0.05%) and arachidonic acid (0.58±0.05%). The fatty acid composition varied little across the samples, except for the Sudanese sesame oil, which contained linoleic and oleic acids in a ratio of 0.93. Sesame oil from the other countries presented an average linolelic:oleic acid ratio of 1.18±0.17 (Fig 3).

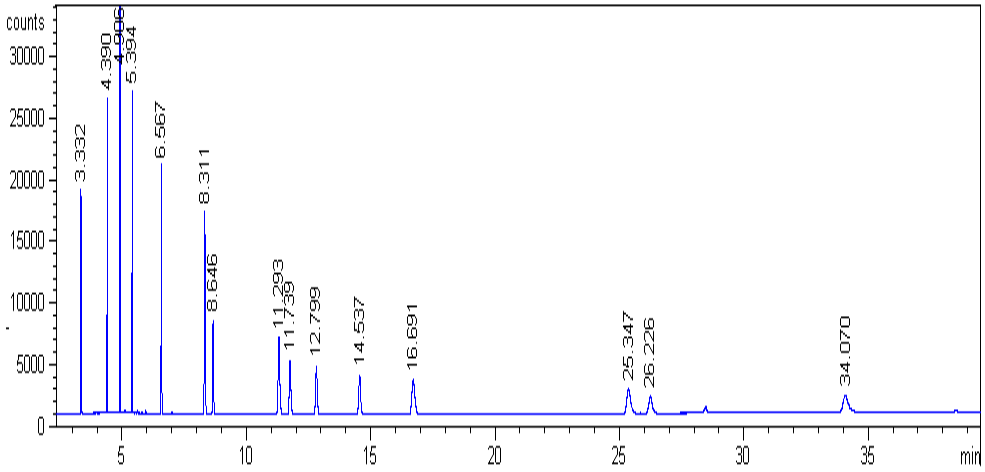

Fig. 1. GC chromatogram of fatty acid methyl ester standards.

Table 6. Retention time of fatty acid methyl ester standards

Fatty acid Methyl ester		Retention Time	Fatty acid Methyl ester		Retention Time
C8:0	Octanoic acid ME	3.332	C18:0	Stearic acid ME	11.293
C10:0	Decanoic acid ME	4.390	C18:1	Oleic acid ME	11.739
C11:0	Undecanoic acid ME(I.S.)	4.906	C18:2	Linoleic acid ME	12.799
C12:0	Lauric acid ME	5.394	C18:3	Linolenic acid ME	14.537
C14:0	Myristic acid ME	6.567	C20:0	Arachidic acid ME	16.691
C16:0	Palmitic acid ME	8.311	C22:0	Behenic acid ME	25.347
C16:1	Palmitoleic acid ME	8.646	C22:1	Erucic acid ME	26.226

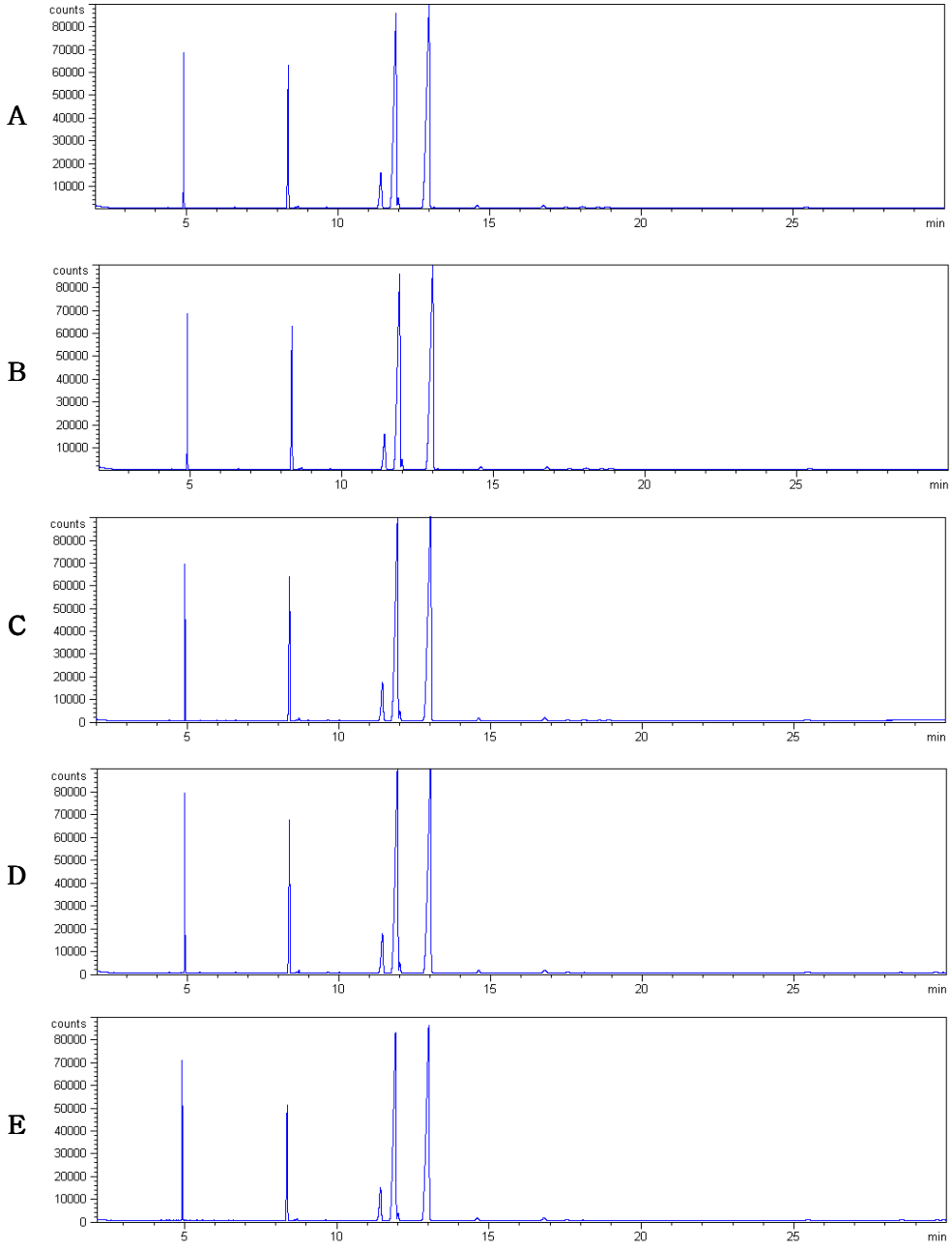

Fig. 2. GC Chromatograms of fatty acid methyl ester in sesame oils. A: India, B: Sudan, C: China, D: Pakistan, E: Korea.

Table 7. Relative composition of fatty acids in sesame oil samples

Fatty acids	Relative composition (%)					
	India	Sudan	China	Pakistan	Korea	Mean
Palmitic acid (C16:0)	11.10 ±1.30[1)]	10.63 ±0.36	10.14 ±0.70	10.54 ±0.15	9.04 ±0.15	10.29 ±0.78
Stearic acid (C18:0)	4.98 ±0.22	6.64 ±0.11	5.09 ±0.12	5.25 ±0.03	5.00 ±0.03	5.39 ±0.71
Oleic acid (C18:1)	38.02 ±0.61	42.26 ±0.28	36.84 ±0.38	39.32 ±0.14	39.38 ±0.17	39.16 ±2.02
Linoleic acid (C18:2)	45.04 ±0.61	39.49 ±0.14	47.02 ±0.20	43.84 ±0.15	45.55 ±0.11	44.19 ±2.86
Linolenic acid (C18:3)	0.34 ±0.01	0.34 ±0.01	0.37 ±0.03	0.43 ±0.12	0.43 ±0.01	0.38 ± 0.05
Arachidic acid (C20:0)	0.53 ±0.08	0.65 ±0.09	0.53 ±0.06	0.62 ±0.08	0.59 ±0.02	0.58 ±0.05

[1)] Mean±standard deviation

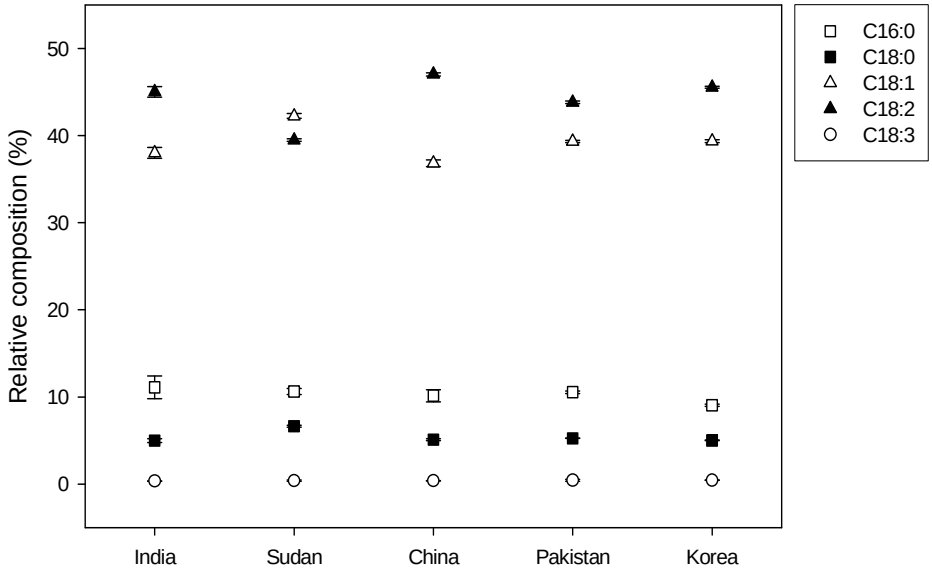

Fig. 3. Comparison of the fatty acid composition in sesame oil samples.

2. *Analysis of sesamin content*

Sesamin content of the various sesame oils was analyzed by HPLC. The chromatogram was the same as shown in Fig. 4, and the standard curve for determining the quantity of sesamin is shown in Fig. 5. The sesamin content of imported and domestic sesame oil is shown in Table 8.

The content of sesamin in sesame oil varied within the range of 4.00 mg/g to 7.82 mg/g. This range is similar to that of 3.69 mg/g to 6.19 mg/g published by Yoo (41). The sesame oil extracted from Chinese sesame seed contained the highest amount of sesamin and sesame oil extracted from Pakistan sesame seed contained the lowest amount of sesamin. These variations in sesamin content may be used as clues to the geographical variation and genetic differences in sesame seeds from different countries.

Table 8. Relative content of sesamin in sesame oil from domestic and imported seed

Sample	Content of sesamin (mg/g)
India	4.85
Sudan	7.00
China	7.82
Pakistan	4.00
Korea	6.38

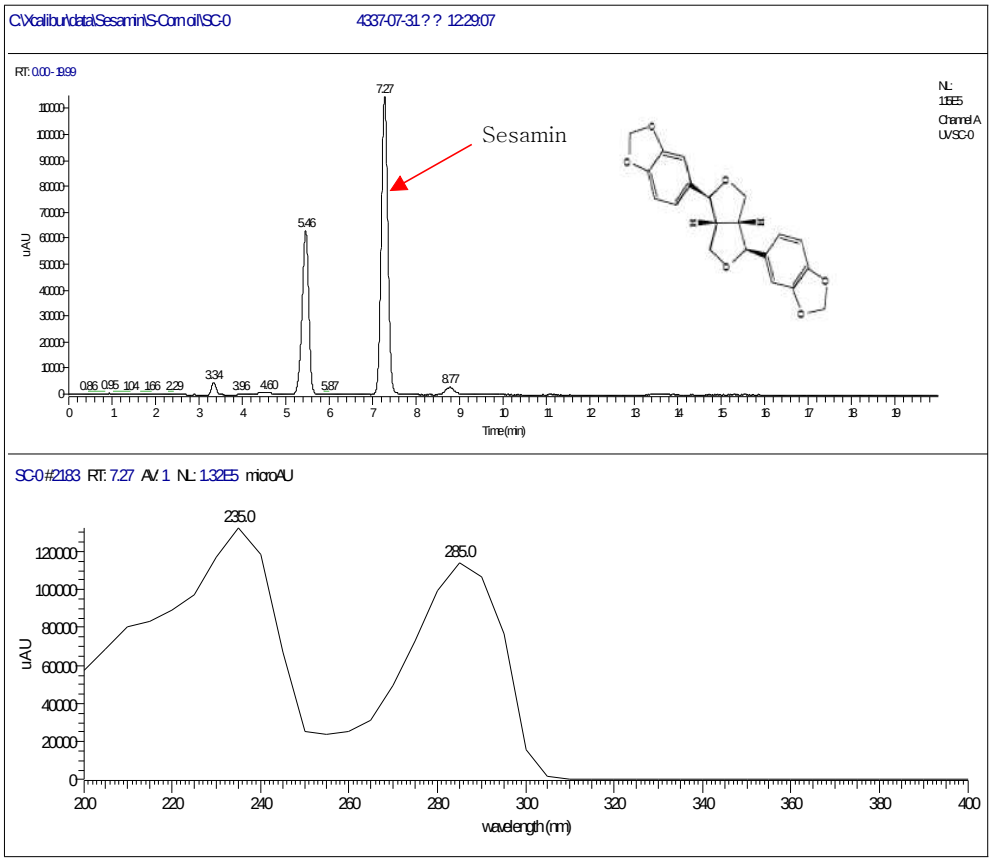

Fig. 4. Chromatogram and UV spectrum of india sesame oil by HPLC analysis.

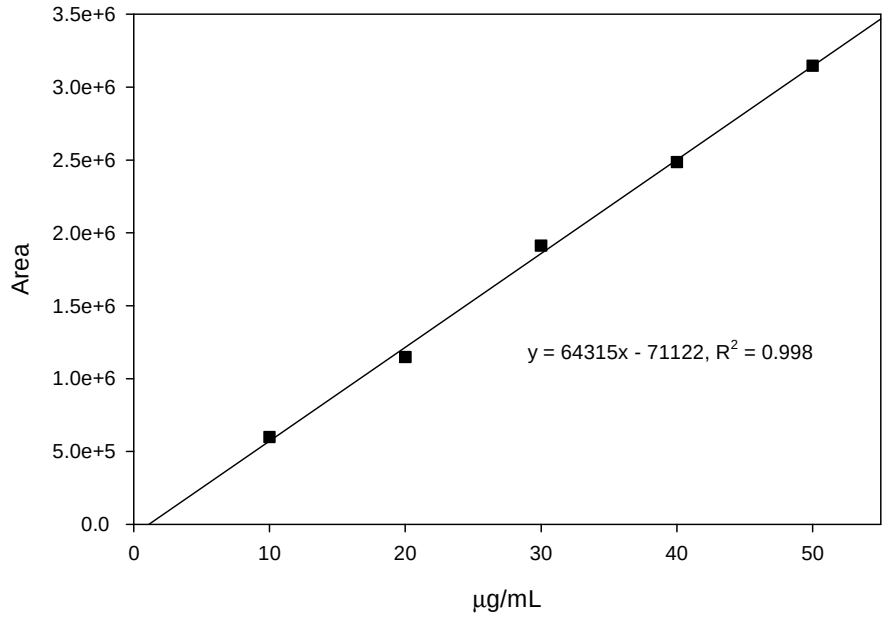

Fig. 5. The Standard curve of sesamin by HPLC analysis.

B. Analysis of fatty acid composition of other vegetable oils

The fatty acid composition of corn oil, soybean oil and rapeseed oil was analyzed by GC (Table 9, Fig. 6.).

1. Fatty acid composition of corn oil

Linoleic acid was the major component (51.74±0.56%) of corn oil, and oleic acid, accounting for 30.82±0.34% was in second place. The saturated fatty acids, palmitic and stearic, were present at 13.69±0.93 and 2.24 ±0.07%, respectively, and linolenic acid was present at 1.02±0.01%. The ratio of saturated to unsaturated fatty acid (P/S) was 5.15.

2. Fatty acid composition of soybean oil

Fatty acids; linoleic acid, palmitic acid, stearic acid and linolenic acid present in soybean oil was contained 55.44±0.52, 21.64±0.28, 11.81±0.48 and 6.27±0.03 respectively. P/S is shown at 5.09 and unsaturated fatty acid was reached at 83.58%.

3. Fatty acid composition of rapeseed oil

Oleic acid, accounting for 62.80±0.10%, was the major fatty acid of rapeseed oil, and linoleic acid and linolenic acid were present at 21.85±0.02 and 6.78±0.14%, respectively. The saturated fatty acids, palmitic and stearic, were present in smaller amounts at 5.33±0.06% and 2.33±0.08%, respectively. The

P/S ratio of rapeseed oil was much higher at 10.97. The fatty acid unique to rapeseed oil, erucic acid ($C_{22:0}$) was also accounted for at 0.21±0.01%

4. Comparison of fatty acid composition of sesame oil and other vegetable oils

Linoleic acid was present in low amounts in sesame oil and corn oil (0.38±0.05% and 1.02±0.01%, respectively), but in high amounts in soybean oil and rapeseed oil (6.27±0.03% and 6.78±0.14%, respectively). The sum of the oleic and linoleic acids in all four oisl averaged 81.91±3.33%. However, the ratio of linoleic acid to oleic acid varied, with a value of 0.89, 0.60, 0.39 and 2.87 in sesame, corn, soybean and rapeseed oil, respectively. The rate of both fatty acids in sesame oil is similar.

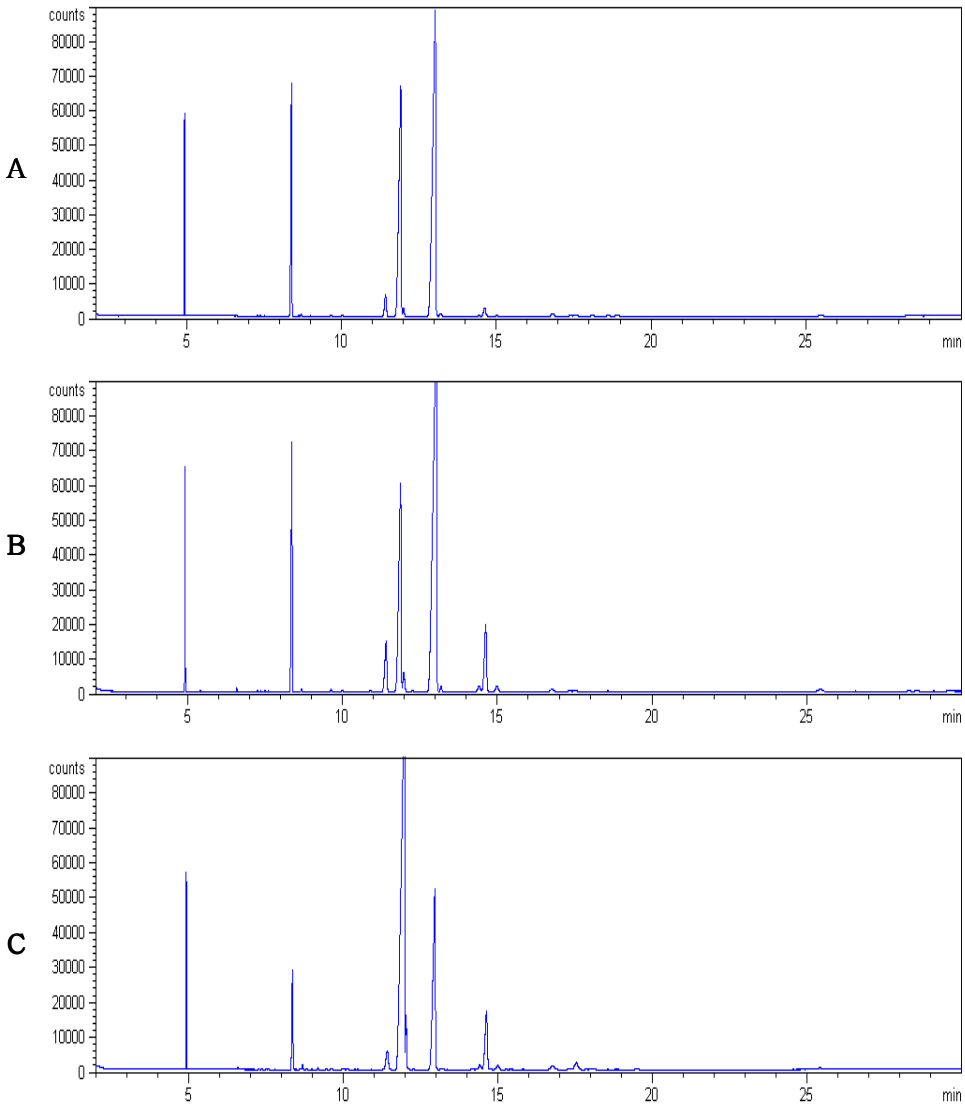

Fig. 6. GC Chromatograms of fatty acid methyl ester in other vegetable oils. A: Corn oil, B: Soybean oil, C: Rapeseed oil.

Table 9. Relative composition of fatty acid in sesame and other vegetable oils

Samples	Relative composition of fatty acid (%)						
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$	$C_{22:1}$
Sesame seed oil	10.29 ±0.78	5.39 ±0.71	39.16 ±2.02	44.19 ±2.86	0.38 ±0.05	0.58 ±0.05	-
Corn oil	13.69 ±0.93	2.24 ±0.07	30.82 ±0.34	51.74 ±0.56	1.02 ±0.01	0.48 ±0.04	-
Soybean oil	11.81 ±0.49	4.49 ±0.06	21.64 ±0.28	55.44 ±0.52	6.27 ±0.03	0.35 ±0.03	-
Rapeseed oil	5.33 ±0.06	2.33 ±0.08	62.80 ±0.10	21.85 ±0.02	6.78 ±0.14	0.69 ±0.04	0.21 ±0.01

C. Analysis of multi detection methods of adulterated sesame oil

1. Detection of other vegetable oils mixed in sesame oil by fatty acid composition

To detect adulterated sesame oil, it was artificially mixed with corn oil, soybean oil and rapeseed oil. Methyl esters of fatty acids were prepared to generalize the experiment and analyzed with GC-FID.

a. Detection of corn oil mixed in sesame oil by fatty acid composition

Corn oil was added to sesame oil up to final concentrations of 5, 10, 15, 20, 30, 40, 50, 75 and 80%. The total fatty acid composition after mixing is shown in Table 10. The contained linoleic acid, oleic acid, palmitic acid, stearic acid and linolenic acid in the order of high quantity in corn oil. While linoleic acid contained higher by 7.6% and oleic acid contained in corn oil was lower by 8.3%. Palmitic acid is contained more 3.4% in corn oil, stearic acid is around twice then sesame oil and as for linolenic acid a little but contained three times higher then sesame oil. Therefore as increasing mixed rate of corn oil, the content of palmitic acid, linoleic acid and linolenic acid increased gradually and content of stearic acid and oleic acid was decreased gradually. In fact, like Fig. 7 as increasing the amount of mixed rate of corn oil, the content of palmitic acid, linoleic acid and linolenic acid were increased linearly and each of the invariable numbers of linear regression (r^2) was separately 0.985, 0.983 and 0.998. On the other hand, the constants of linear regression (r^2) of stearic acid and oleic acid was getting

less /at 0.990 and 0.970 in a straight line. Accordingly, to detect corn oil mixed in sesame oil, analysis of these fatty acids can be used (Fig. 7). By the mixed rate of corn oil, the content of palmitic acid, linoleic acid and linolenic acid were increased and others fatty acid content in the rate of mixed rate of corn oil was gradually decreased which could be useful tool to judge the adulterated sesame oil.

The ratio of C18:1+C18:2/C16:0×C18:3 could be useful for distinguishing sesame oil and corn oil, since it is quite different between the two. The difference in the content of palmitic acid alone is not possible when it constitutes 5% or less of the mixed sample due to the wide extent of the ratio C18:1+C18:2/C16:0×C18:3. It could also be difficult to determine a correlation formula on account of the C18:1+C18:2/C16:0×C18:3 ratio decreasing consecutively. An other ratio; C16:0×C18:2×C18:3/C18:0+C18:1, used all five fatty acids. When these fatty acids were used, predicted mixed ratio was the most accurate. Depending on mixed rate of corn oil, the ratio of fatty acid composition was shown to the increase in a straight line (r^2=0.989), and it fit the formula, y=0.1611x+ 2.9114 (Fig. 8).

In conclusion, based on the differences in fatty acid composition, the percent of adulteration of sesame oil can be determined with certainty, but when the corn oil was mixed at less than 5% the exact amount couldn't be estimated. Therefore, to estimate more precisely the percent adulteration of sesame oil, we investigated the additional analysis methods that are described later.

Table 10. Fatty acid composition of sesame oils mixed with commercial corn oil

Concentration of corn oil (v/v %)	Relative composition of fatty acid (%)					
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$
0	10.29 ±0.78[1)]	5.39 ±0.71	39.16 ±2.02	44.19 ±2.86	0.38 ±0.05	0.58 ±0.05
5	10.65 ±0.41	4.76 ±0.20	37.86 ±0.23	45.80 ±0.32	0.37 ±0.00	0.55 ±0.04
10	11.10 ±0.79	4.57 ±0.13	37.30 ±0.44	46.09 ±0.36	0.41 ±0.01	0.53 ±0.05
15	11.41 ±0.66	4.53 ±0.33	36.88 ±0.28	46.16 ±0.87	0.46 ±0.01	0.56 ±0.06
20	11.44 ±0.78	4.32 ±0.13	36.64 ±0.37	46.62 ±0.42	0.47 ±0.02	0.52 ±0.05
30	12.45 ±1.34	4.34 ±0.55	34.88 ±1.89	47.24 ±0.53	0.54 ±0.01	0.55 ±0.09
40	12.55 ±1.02	3.81 ±0.20	33.91 ±1.78	48.59 ±1.47	0.63 ±0.02	0.51 ±0.06
50	13.14 ±2.42	3.44 ±0.06	34.17 ±1.10	48.13 ±1.12	0.67 ±0.02	0.46 ±0.13
75	13.14 ±0.37	2.92 ±0.11	32.13 ±0.94	50.45 ±0.64	0.85 ±0.02	0.50 ±0.01
80	13.60 ±1.12	2.76 ±0.10	31.64 ±0.97	50.65 ±0.96	0.89 ±0.02	0.47 ±0.05
100	13.69 ±0.93	2.24 ±0.07	30.82 ±0.34	51.74 ±0.56	1.02 ±0.01	0.48 ±0.04

[1)]Mean±Standard deviation

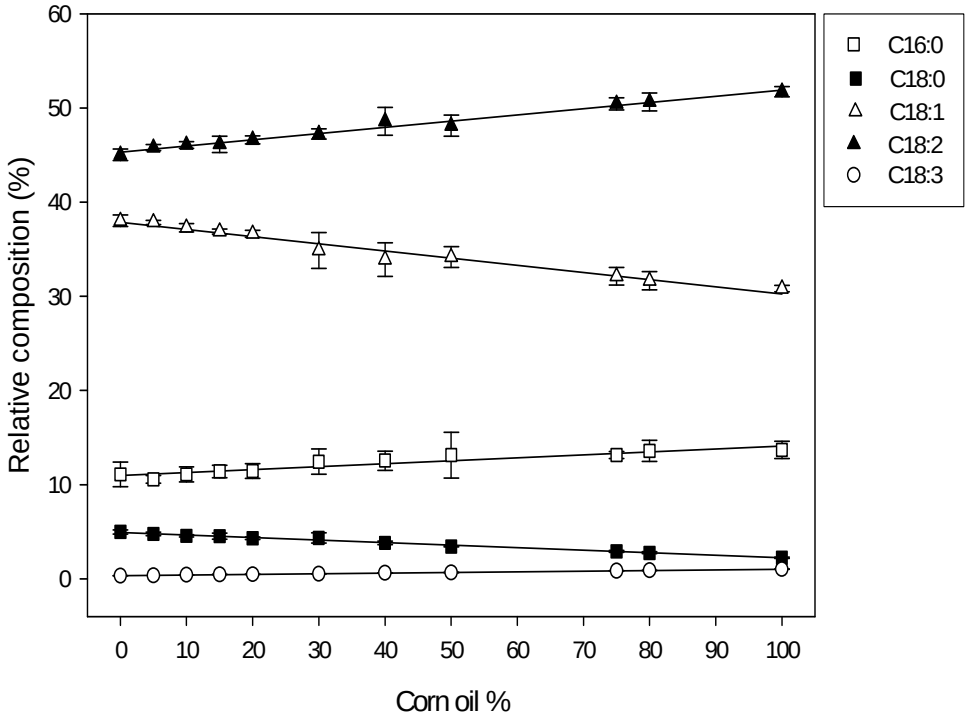

Fig. 7. Changes of major fatty acid contents in sesame oils mixed with corn oil.

Table 11. Application of discrimination index in sesame oils

Samples	O+L/P×Ln[1)]	L/O	P+L+Ln/S+O	P×L×Ln/S+O
India	22.49±3.34[2)]	1.18±0.01	1.31±0.04	3.92±0.54
Sudan	22.65±0.13	0.93±0.01	1.03±0.02	2.92±0.01
China	22.29±1.73	1.28±0.01	1.37±0.03	4.24±0.34
Pakistan	21.50±0.72	1.12±0.01	1.23±0.01	3.82±0.14
Korea	21.69±0.54	1.16±0.01	1.24±0.01	4.02±0.12

[1)]P: Palmitic acid($C_{16:0}$), S: Stearic acid($C_{18:0}$), O: Oleic acid($C_{18:1}$), L: Linoleic acid($C_{18:2}$), Ln: Linolenic acid($C_{18:3}$)

[2)]Mean±Standard deviation

Table 12. Discrimination index of adulterating sesame oils with corn oil by fatty acid composition

Concentration of corn oil (v/v %)	O+L/P×Ln[1)]	L/O	P+L+Ln/S+O	P×L×Ln/S+O
5	21.26±0.95	1.21±0.00	1.33±0.01	4.23±0.15
10	18.85±1.21	1.24±0.01	1.38±0.02	4.96±0.29
15	15.96±0.75	1.25±0.02	1.40±0.02	5.80±0.12
20	15.65±0.90	1.27±0.00	1.43±0.02	6.07±0.28
30	12.41±1.64	1.31±0.00	1.49±0.04	7.49±0.71
40	10.55±1.03	1.37±0.01	1.58±0.05	9.53±1.03
50	9.58±1.72	1.41±0.01	1.65±0.08	11.16±1.78
75	7.37±0.32	1.57±0.06	1.84±0.07	16.16±1.18
80	6.86±0.59	1.60±0.07	1.89±0.07	17.76±1.51
100	5.91±0.39	1.68±0.00	2.01±0.03	21.92±1.22

[1)]P: Palmitic acid($C_{16:0}$), S: Stearic acid($C_{18:0}$), O: Oleic acid($C_{18:1}$), L: Linoleic acid($C_{18:2}$), Ln: Linolenic acid($C_{18:3}$)

[2)]Mean±Standard deviation

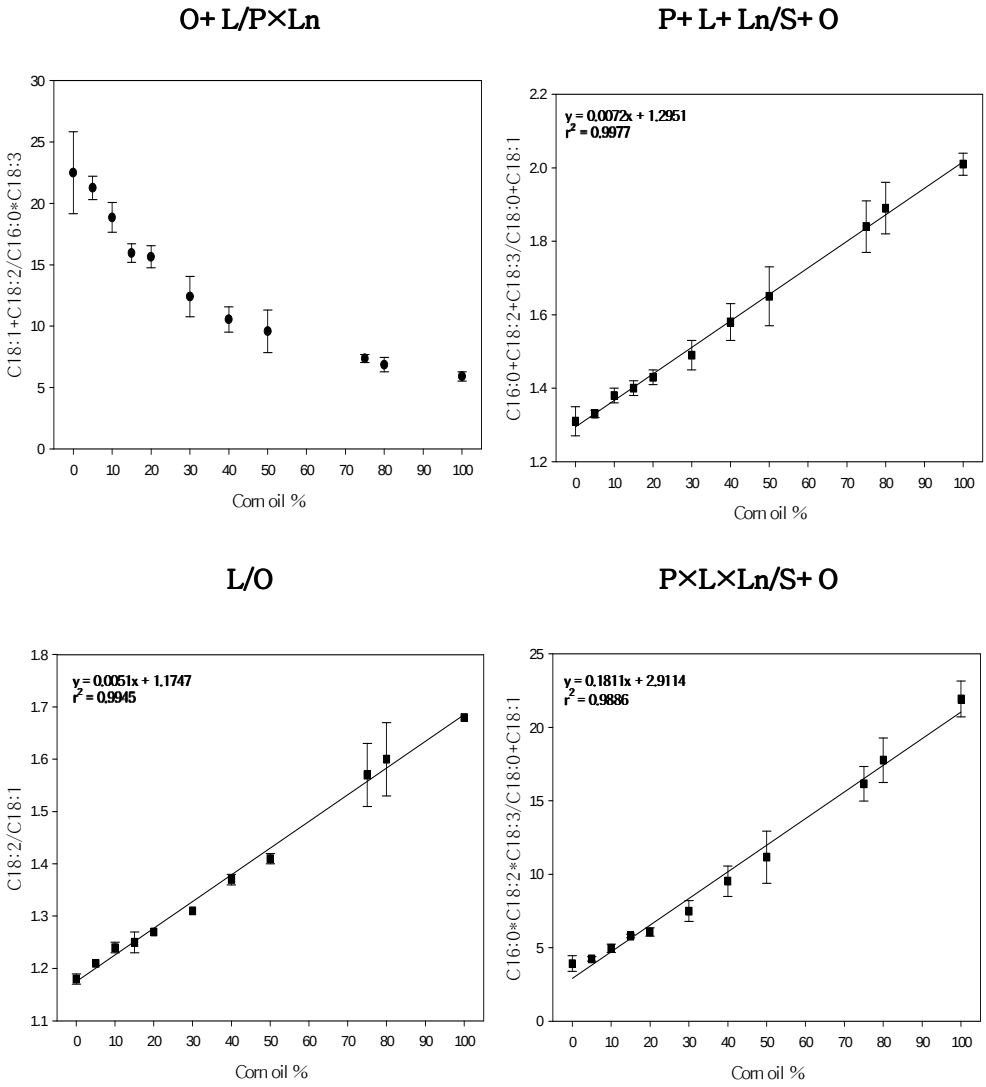

Fig. 8. Correlation of fatty acid ratio and concentration of corn oil as discrimination index. P: Palmitic acid(C16:0), S: Stearic acid(C18:0), O: Oleic acid(C18:1), L: Linoleic acid(C18:2), Ln: Linolenic acid(C18:3).

b. Detection of soybean oil mixed in sesame oil by fatty acid composition

Sesame oil obtained from Indian seeds was adulterated by soybean oil produced by H corporation at the rate of 5, 10, 20, 40 and 80%. The fatty acid composition of the samples was analyzed and is shown in Table 13.

In the case of soybean oil, the major fatty acid components were oleic acid and linoleic acid. Like soybean oil, sesame oil also contained linolenic acid in high amount. Looking up the content of each of the fatty acids, it was found that palmitic acid is present at 0.2% in sesame oil, which is higher than in soybean oil. Also, stearic acid, oleic acid and linoleic acid are present in sesame oil at 0.51%, 16.24%, and 11.2% less, respectively, than soybean oil. Especially, linolenic acid is 5.93% higher in the GC chromatogram of sesame oil, such that the difference in peak size is visible to the naked eye. It was seen that increasing the percent of soybean oil, increases the content of palmitic acid and, linolenic acid and the decreases the content of stearic acid, oleic acid, linoleic acid. The content of palmitic acid, linoleic acid and linolenic acid was shown to increase linearly with a regression constant (r^2) of 0.652, 0.999 and 1, respectively (Fig. 8). The linoleic acid content decreased linearly with increasing amounts of soybean oil with a regression constant of 0.998 (Fig. 9).

As linolenic acid in sesame oil was increased by different ratio by mixing different proportion of soybean oil, it is considered that the presumption of mixing soybean oil in increasing the content of linolenic acid would be possible.

Certain fatty acid composition of soybean oil infer oil quality, as shown in Table 14 and Fig. 10. Measuring fatty acid content in edible oils was done using the ratios $C_{18:1}+C_{18:2}/C_{16:0}\times C_{18:3}$, $C_{18:1}/C_{18:2}$, $C_{18:2}/C_{18:1}$, $C_{18:1}\times C_{18:3}/C_{18:2}$ which would determined the inferred quality of soybean oil and sesame oils.

Thus, adulteration of sesame oil by mixing with soybean oil can be detected by using the formula ① y=-0.0044x+0.8334, and for the purpose of content comparision of linoleic acid, ② the ratio of $C_{18:1}/C_{18:2}$.

Table 13. Fatty acid composition of sesame oils mixed with commercial soybean oil

Concentration of soybean oil (v/v %)	Relative composition of fatty acid (%)					
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$
0	10.29 ±0.78[1)]	5.39 ±0.71	39.16 ±2.02	44.19 ±2.86	0.38 ±0.05	0.58 ±0.05
5	10.71 ±0.70[1)]	4.91 ±0.12	37.22 ±0.40	46.03 ±0.20	0.65 ±0.10	0.49 ±0.01
10	10.37 ±0.20	4.99 ±0.26	36.75 ±0.80	46.41 ±0.45	0.92 ±0.01	0.56 ±0.90
20	10.31 ±0.02	4.95 ±0.90	35.08 ±0.52	47.56 ±0.40	1.55 ±0.03	0.55 ±0.01
40	11.03 ±0.45	4.78 ±0.60	31.80 ±1.00	49.23 ±0.02	2.68 ±0.06	0.48 ±0.10
80	11.45 ±0.06	4.61 ±0.80	25.37 ±0.90	53.12 ±0.01	5.06 ±0.41	0.39 ±0.10
100	11.81 ±0.49	4.49 ±0.06	21.64 ±0.28	55.44 ±0.52	6.27 ±0.03	0.35 ±0.03

[1)]Mean±Standard deviation

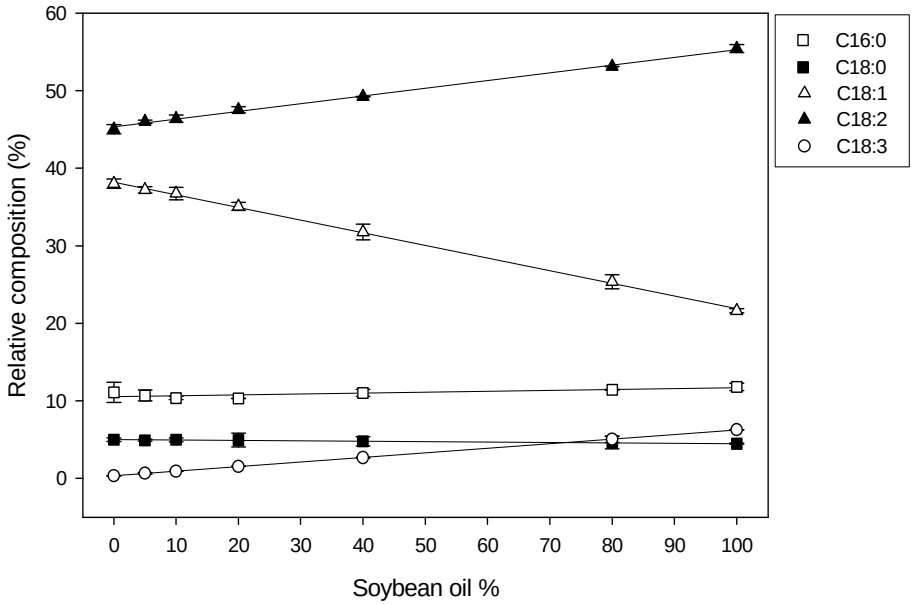

Fig. 9. Changes of major fatty acid contents in sesame oils mixed with soybean oil.

Table 14. Discrimination index of adulterating sesame oils with soybean oil

Concentration of soybean oill (v/v %)	O+L/P×Ln[1)]	L/O	O/L	O×Ln/L
5	11.96 ±2.95[2)]	1.24 ±0.01	0.81 ±0.02	0.53 ±0.01
10	8.17 ±3.00	1.26 ±0.01	0.79 ±0.02	0.73 ±0.12
20	5.17 ±0.01	1.36 ±0.06	0.74 ±0.01	1.14 ±0.04
40	2.74 ±1.20	1.55 ±0.20	0.65 ±0.03	1.73 ±0.1
80	1.35 ±1.23	2.09 ±0.15	0.48 ±0.03	2.42 ±0.04
100	1.04 ±0.05	2.56 ±0.05	0.39 ±0.01	2.45 ±0.04

[1)]P: Palmitic acid($C_{16:0}$), S: Stearic acid($C_{18:0}$), O: Oleic acid($C_{18:1}$), L: Linoleic acid($C_{18:2}$), Ln: Linolenic acid($C_{18:3}$)

[2)]Mean±Standard deviation

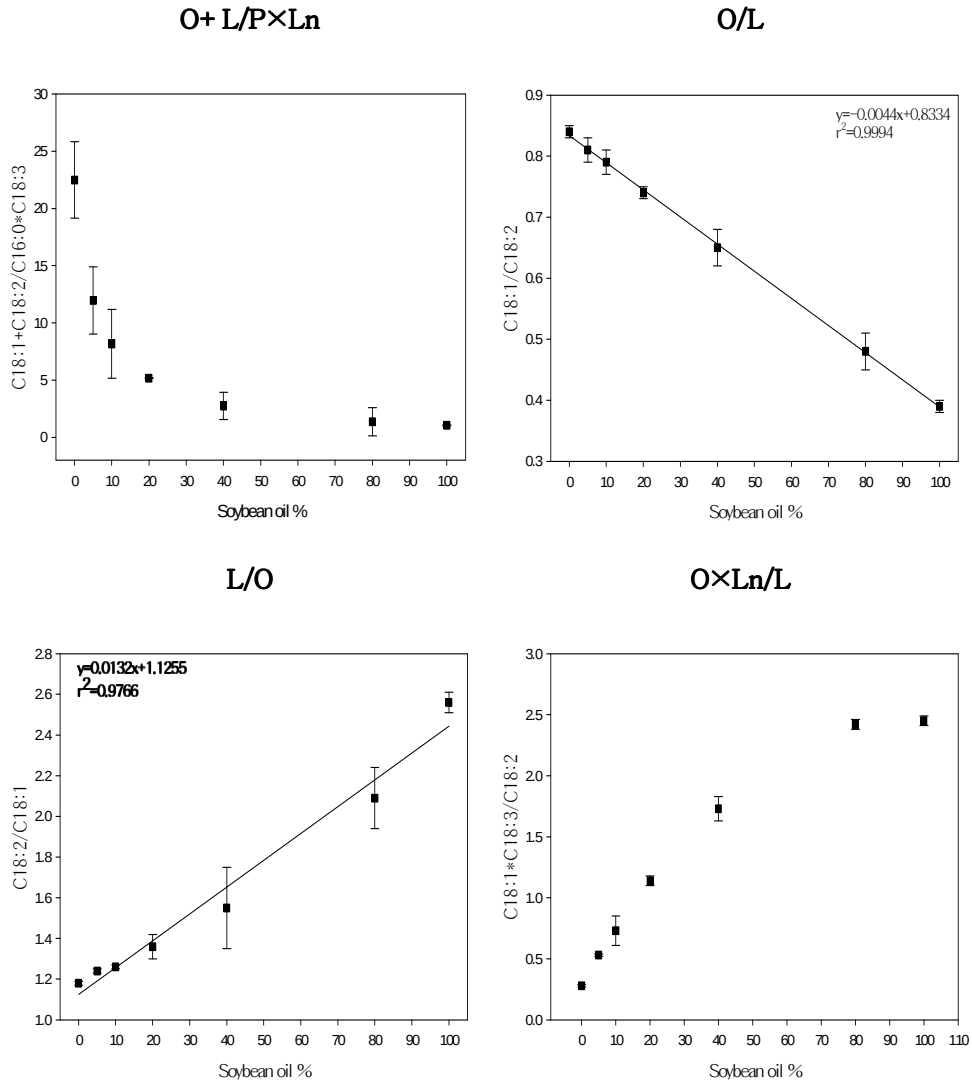

Fig. 10. Correlation of fatty acid ratio and concentration of soybean oil as discrimination index. P: Palmitic acid(C16:0), S: Stearic acid(C18:0), O: Oleic acid(C18:1), L: Linoleic acid(C18:2), Ln: Linolenic acid(C18:3).

c. Detection of rapeseed oil mixed in sesame oil by fatty acid composition

Sesame oil obtained from Indian seeds was adulterated by rapeseed oil produced by H corporation at the rate of 5, 10, 20, 40 and 80%. The fatty acid composition of the above samples was analyzed and is shown in Table 15.

The content of fatty acids such as oleic acid, erucic acid and linoleic acid in the mixtures was higher than the fatty acid composition of rapeseed oil. Oleic acid is present in sesame oil at 37.88±0.45%, but is in rapeseed oil at 62.80±0.10%. Erucic acid, which is not present in sesame oil, was detected in mixtures at 0.21±0.01%.The amounts of palmitic acid, stearic acid and linoleic acid were reduced by 5.99%, 2.67% and 23.11% respectively, in the mixtures. Meanwhile, oleic acid, erucic acid and linolenic acid increased by 24.92%, 6.44% and 0.21%, respectively. As the amount of rapeseed oil in the mixtures increased, the constant (r^2) of linear regression for oleic acid, linolenic acid and erucic acid also increased and pointed at 0.999, 0.999 and 0.957, respectively. Likewise, the constant (r^2) of linear regression for palmitic acid, stearic acid and linoleic acid decreased at 0.993, 0.996 and 0.998, respectively (Fig 10).

The of 0.04±0.02% erucic acid in adulterated sesame oil is most likely due to the mixing of rapeseed oil by 5%; all other results will be according to Table 15. The characteristic fatty acids of rapeseed oil, presuming a high discrimination index, are shown in Table 14 and Fig. 12. Discrimination indices were determined from the rations $C_{18:1}+C_{18:2}/C_{16:0}\times C_{18:3}$, $C_{18:1}/C_{18:2}$,

$C_{18:2}/C_{18:1}$ and $C_{18:1}\times C_{18:3}/C_{18:2}$. As in the case of sesame oil mixed with soybean oil, as the amount of rapeseed oil increased the mixture was reduced in the ratios $C_{18:1}+C_{18:2}/C_{16:0}\times C_{18:3}$ and $C_{18:1}/C_{18:2}$ and increased in the ratio $C_{18:2}/C_{18:1}$, $C_{18:1}\times C_{18:3}/\ C_{18:2}$ (Table 17).

These results indicated that the amount of rapeseed oil mixed with sesame oil can be determined by the relative amounts of erucic acid and linolenic acid in the mixture. Thus, comparison of the content of erucic and linolenic acids could be a useful tool for identifying sesame oil adulterated with rapeseed oil.

Table 15. Fatty acid composition of sesame oils mixed with commercial rapeseed oil

Concentration of rapeseed oil (v/v %)	Relative composition of fatty acid (%)						
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$	$C_{22:1}$
0	10.29 ±0.78[1)]	5.39 ±0.71	39.16 ±2.02	44.19 ±2.86	0.38 ±0.05	0.58 ±0.05	-
5	10.65 ±0.47[1)]	4.82 ±0.08	39.07 ±0.25	44.22 ±0.11	0.67 ±0.01	0.53 ±0.06	0.04 ±0.02
10	10.07 ±0.20	4.78 ±0.04	40.27 ±0.12	43.31 ±0.06	0.93 ±0.01	0.59 ±0.03	0.06 ±0.03
20	9.96 ±1.14	4.43 ±0.15	42.77 ±0.65	40.56 ±0.23	1.66 ±0.03	0.57 ±0.08	0.06 ±0.01
40	8.63 ±0.40	4.07 ±0.06	46.98 ±0.25	36.87 ±0.04	2.73 ±0.02	0.63 ±0.04	0.10 ±0.02
80	6.70 ±0.69	2.93 ±0.08	57.21 ±0.36	27.00 ±0.06	5.39 ±0.13	0.57 ±0.20	0.15 ±0.09
100	5.33 ±0.06	2.33 ±0.08	62.80 ±0.10	21.85 ±0.02	6.78 ±0.14	0.69 ±0.04	0.21 ±0.01

[1)]Mean±Standard deviation

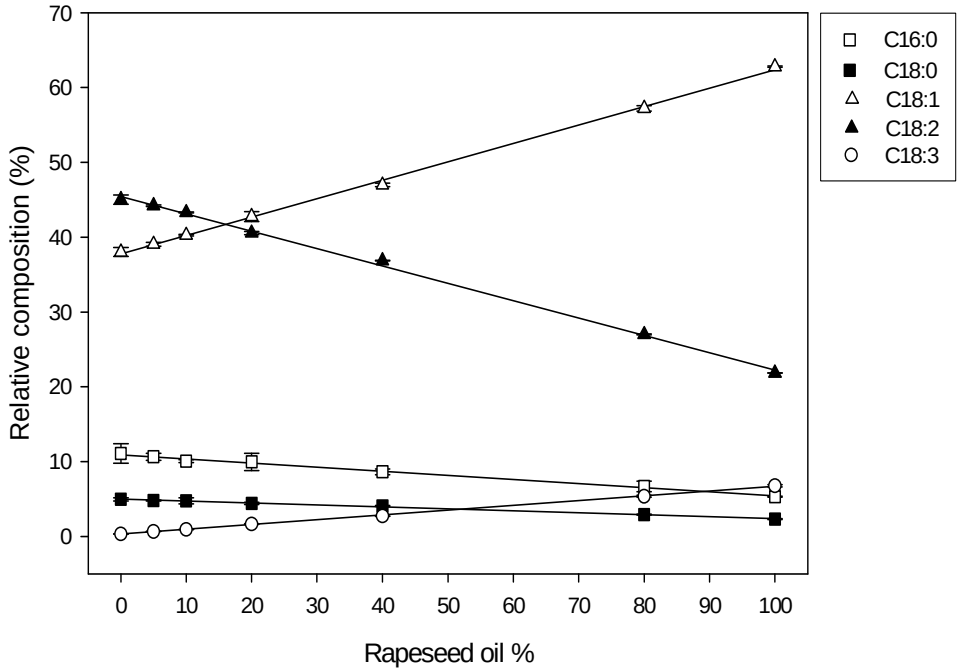

Fig. 11. Changes of major fatty acid contents in sesame oils mixed with rapeseed oil.

Table 16. Discrimination index of adulterating sesame oils with rapeseed oil

Concentration of rapeseed oil (v/v %)	O+L/P×Ln[1)]	L/O	O/L	O×Ln/L
5	11.64 ±0.52[2)]	1.13 ±0.01	0.88 ±0.00	0.59 ±0.00
10	8.96 ±0.13	1.08 ±0.00	0.93 ±0.00	0.86 ±0.01
20	5.08 ±0.52	0.95 ±0.01	1.05 ±0.01	1.75 ±0.04
40	3.57 ±0.16	0.78 ±0.00	1.27 ±0.01	3.47 ±0.03
80	2.35 ±0.18	0.47 ±0.00	2.12 ±0.02	11.41 ±0.37
100	2.34 ±0.06	0.35 ±0.00	2.87 ±0.01	19.49 ±0.36

[1)]P: Palmitic acid($C_{16:0}$), S: Stearic acid($C_{18:0}$), O: Oleic acid($C_{18:1}$), L: Linoleic acid($C_{18:2}$), Ln: Linolenic acid($C_{18:3}$)

[2)]Mean±Standard deviation

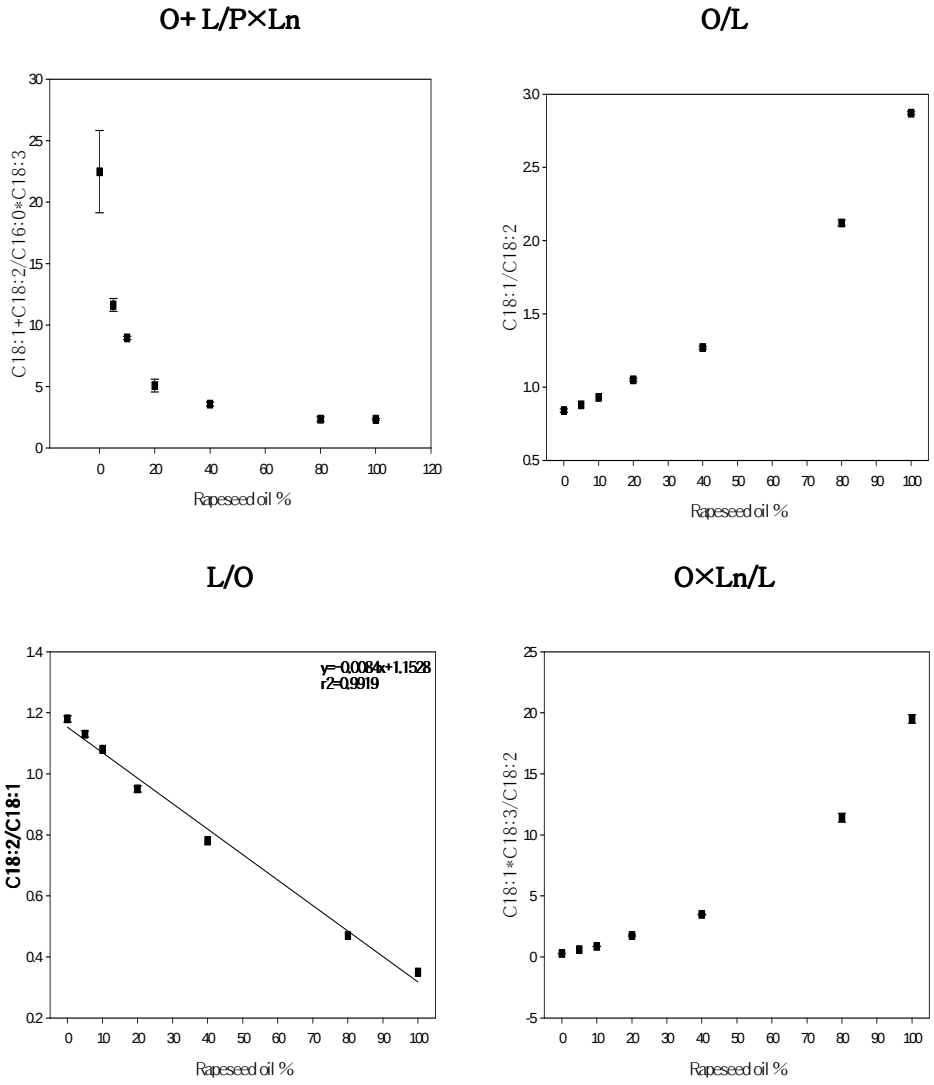

Fig. 12. Correlation of fatty acid ratio and concentration of rapeseed oil as discrimination index.

2. Detection of the other vegetable oil mixed in sesame oil by analysis of sesamin content

The detection of sesamin by HPLC was used to observe changes in sesamin content and the possibility of differentiating pure sesame oil from a mixture was examined.

Table 17 shows how sesamin content changed as a function of the percent of edible oil in the sesame oil Fig. 13 shows the good correlation (r^2=0.996) between the sesamin content and the purity of sesame oil. It was identified that interruption material is not made by adding the other edible oil, and the result was the same result in adding corn oil, soybean oil and rapeseed oil.

It is shown to make a good correlation (r^2=0.996) between the sesamin content and the mixture ratio of sesame oil. Analysis of sesamin content by HPLC method was not applicable to sesame oils of certain origins due to various ranges of sesamin contents (within the limit of 4.00 mg/g to 7.82 mg/g). Roasting conditions a make a small difference in the sesamin content of the oils.

Table 17. Relative content of sesamin in sesame oil mixed with other vegetable oils (mg/g)

Adultant / Mixing %	Corn oil	Soybean oil	Rapeseed oil
5	4.61	4.53	4.15
10	4.23	4.40	4.00
15	3.9	-	-
20	3.85	3.81	3.96
30	3.41	-	-
40	2.85	2.93	3.17
50	2.45	-	-
75	1.11	-	-
80	0.90	1.03	1.04
100	0	0	0

[1)]SC: sesame oil mixed corn oil, SS: sesame oil mixed soybean oil, SR: sesame oil mixed rapeseed oil

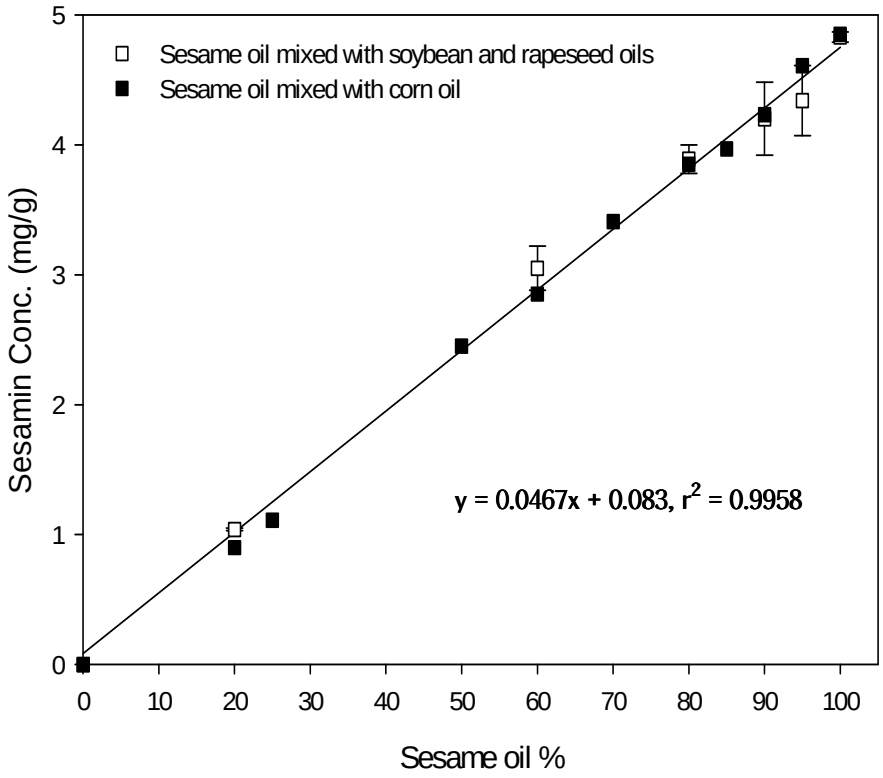

Fig. 13. Correlation of relative content of sesamin and concentration of sesame oil.

3. Detection of other vegetable oils mixed in sesame oil by carbon isotope ratio

Plants use either the Calvin (C_3) or Hatch & Slack (C_4) pathway for photosynthetic carbon dioxide fixation, as revealed by differences in both leaf anatomy and $^{13}C/^{12}C$ ratios. Plants using the C_3 cycle make 3-phosphoglycerate as the first product of photosynthesis, while in plants using the C_4 cycle, oxalacetate, malate and aspartate are the initial products. Recently, practical use has been mades of the finding that the $^{13}C/^{12}C$ ratio of a plant derived material reflects the photosynthetic pathway operating in the plant from which it was derived (42,43). Because corn plant use the C_4 pathway, and sesame plants use the C_3 (44), the $^{13}C/^{12}C$ ratio in adulterated sesame oils and pure sesame oil have been compared in this research.

Mixing ratios of corn oil in adulterated sesame oil were 0, 5, 10, 15, 20, 30, 40, 50, 75, 80 and 100% (v/v). Analysis of isotope ratios was investigatedas a possible method for detection of adulterated sesame oil (Table 18, 19).

Analysis of carbon isotope ratios in sesame oil from different countries yielded a δ13C/12C value of -28.56‰ and a measured range of -27.68 ~ -29.26‰. In contrast, the carbon isotope ratio was -16.89±0.38‰ in corn oil. When sesame oil was adulterated with corn oils, the linear regression constant (r^2) was 0.996 and a simple equation of y=0.1183x-28.872 was established (Fig. 14).

These large differences in carbon isotope ratio between sesame oil and corn oil could be used to determine the adulteration of both oils. However, the detection of mixture is only possible up to certain limit. When the adulteration is be less than 10%, the detection of adulteration is very difficult.

Table 18. Carbon isotope ratio of sesame oils

Samples	Isotope ratio (‰)
India	-28.61±0.60[1)]
Sudan	-27.68±0.44
China	-28.45±1.01
Pakistan	-28.78±0.11
Korea	-29.26±0.90

[1)]Mean±Standard deviation

Table 19. Carbon isotope ratio of India sesame oils mixed with corn oil

Concentration of corn oil (v/v %)	Isotope ratio (‰)
0	-28.61±0.60[1)]
5	-28.37±0.26
10	-27.93±0.44
15	-26.63±0.04
20	-26.51±0.22
30	-25.76±0.17
40	-24.03±0.12
50	-23.22±0.44
75	-19.84±0.43
80	-19.53±0.52
100	-16.89±0.38

[1)]Mean±Standard deviation

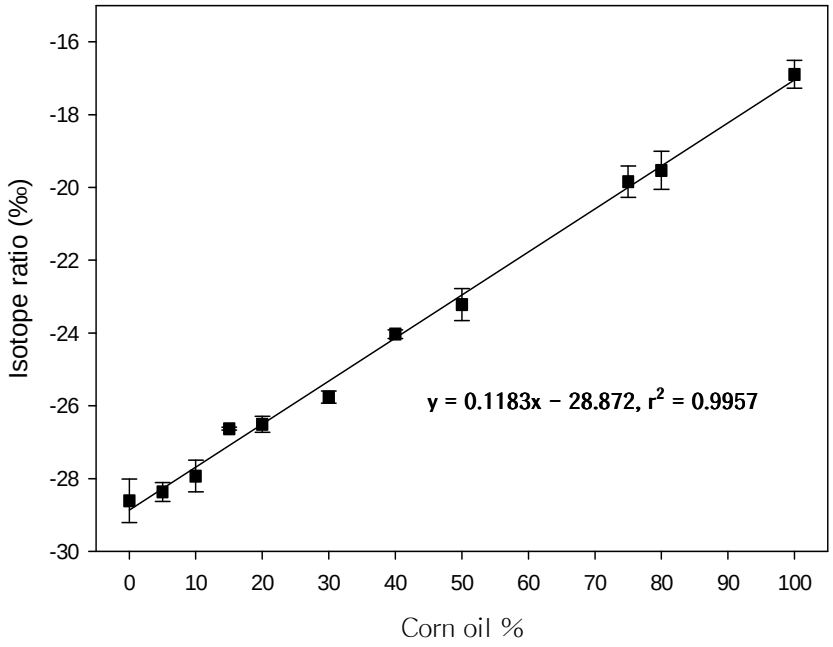

Fig. 14. Correlation of carbon isotope ratio and concentration of corn oil.

4. Detection of other vegetable oils mixed in sesame oil by NIR

Near-infrared reflectane (NIR) is used worldwide for the rapid quantitative determination of moisture, lipid, protein, carbohydrates and fiber in cereals, grains, feeds, meats and dairy products (45-50). Therefore, adulteration of sesame oil using near-infrared reflectance (NIR) was determined.

Fig. 15 shows the NIR spectrum of sesame oilof various of origins. This result shows the rapid determination of purity of vegetable oils from different countries.

NIR absorbance spectra were collected at 1650～1790 nm, 1920～2000 nm and 2250～2450 for sesame oils of different origin (Fig. 16,17) and at 1650～1800 nm, 1950~2000 nm, 2150~2200 nm and 2350~2450 nm for sesame oil and other vegetable oils (corn oil, soybean oil and rapeseed oil). The principal difference between the spectra was at 400~700 nm in VIS and was mainly related to color. Although sesame oil tends to be more deep and dark than other edible oils, the roasting conditions during its manufacture can produce different colors. Conclusively, NIR spectroscopy is useful for screening the geographical origin of sesame oils and other vegetable oils but is not useful for detection of adulterated sesame oil.

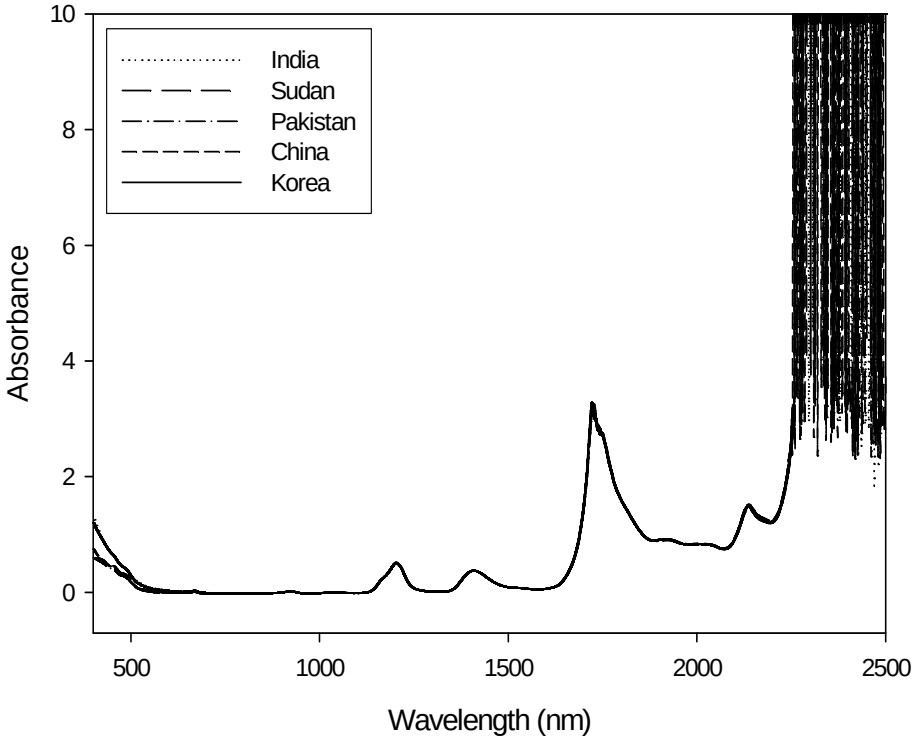

Fig. 15. NIR spectra of sesame oils.

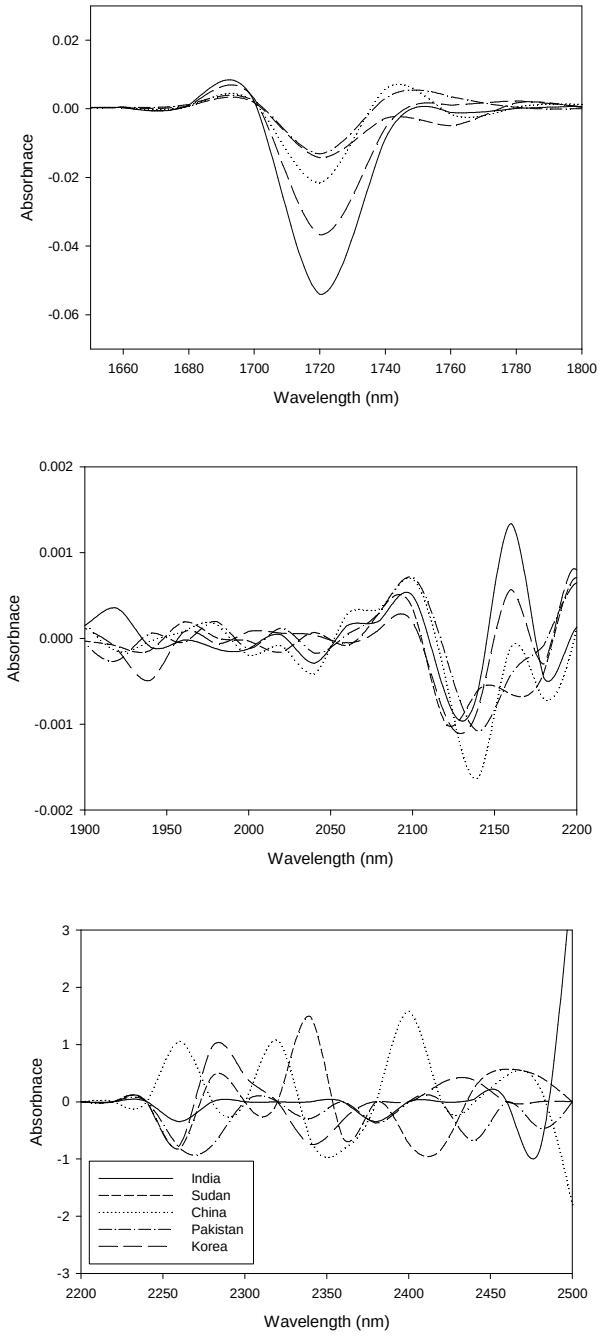

Fig. 16. NIR second derivative spectra of sesame oils by sesame seed origin.

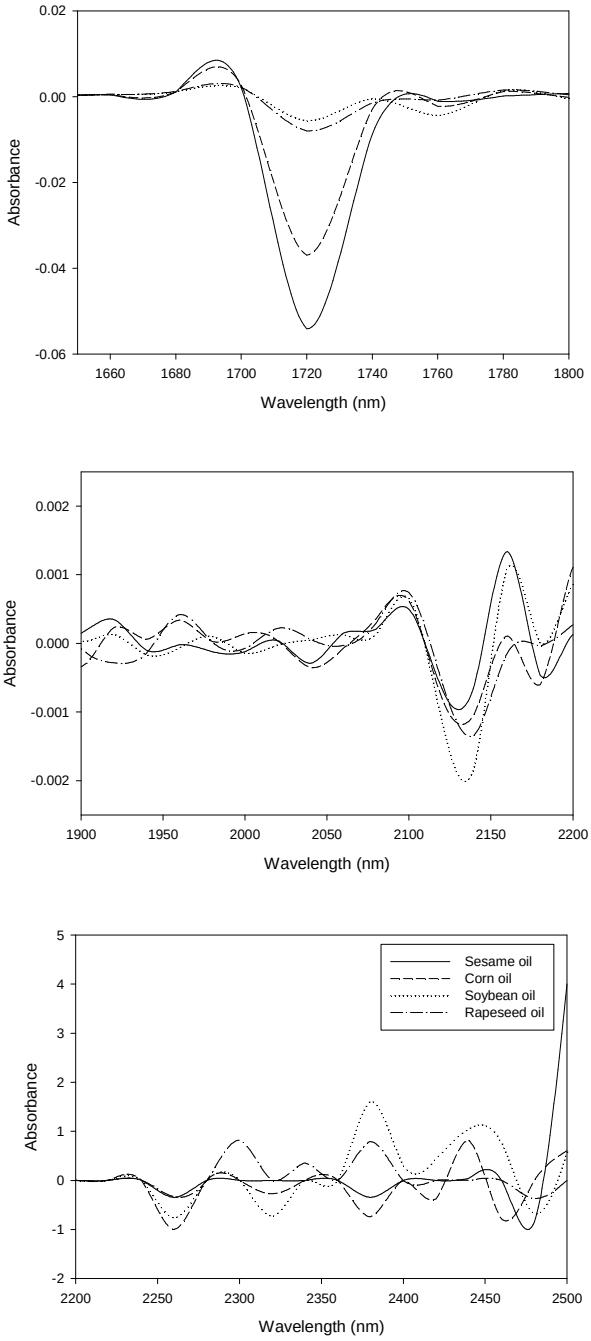

Fig. 17. NIR second derivative spectra of other vegetable oils.

5. Detection of other vegetable oil mixed in sesame oil by volatile organic components

Analysis of volatile organic components by GC/MS could be another possible method to detect the adulteration of sesame oil.

a. Analysis of volatile organic components of sesame oil

Volatile organic components were extracted, from sesame oil that originated from different countries (India, Sudan, China and Korea) using SDE (simultaneous steam distillation and extraction) apparatus and then concentrated. Volatile organic components were analyzed using gas chromatography/mass spectrometry (GC/MS). The gas chromatograms are shown in Fig. 18 and their concentrations are given in Table 20. Total 53 components were identified in sesame oil imported from India, while 35 and 30 were identified in sesame seed oils imported from Sudan and China, respectively. 42 components were identified in the Korean sample.

In Indian sesame oil the volatile organic components were consisted of 16 N-compounds, 7 alcohols, 11 aldehydes, 4 hydrocarbons, 6 S-compounds, 2 esters, 4 ketones and 3 miscellaneous. The relative area obtained for each functional group was N-compounds (46.65%), alcohols (29.26%), aldehydes (7.80%), hydrocarbons (4.58%), S-compounds (3.74%), esters (3.51%), ketones (1.40%) and miscellaneous (3.06%). The major volatile organic components were 2,5-dimethyl pyrazine (9.61%), 2,3-dimethyl-5-ethyl pyrazine (9.12%), trimethyl pyrazine (5.37%), 2-ethyl-6-methyl pyrazine (3.79%). The formation of pyrazine compounds in many thermally processed foods results from

Maillard-type nonenzymatic reactions between reducing sugars and free amino acid or amides, which reduces the amounts a number of 2,5- and 2,6-dimethyl pyrazine (51,52). Roasting is the most significant step in coffee, nut and bean processing, and causes important physical, chemical, and structural changes in the products(52-57).

In Sudanese sesame oil, the volatile organic components were identified and categorized as 13 N-compounds, 4 alcohols, 9 aldehydes, 3 hydrocarbons, 1 S-compounds, 2 esters and 3 miscellaneous. Pyrazine derivatives of unique flavor components of sesame oil constituted the major components at 31.62%.

In Chinese sesame oil the volatile organic components were identified and categorized as 11 N-compounds (25.36%), 3 alcohols (40.03%), 8 aldehydes (26.48%), 1 hydrocarbon (1.01%), 1 S-compound (0.35%), 2 esters (5.01%), 1 ketone (0.13%) and 3 miscellaneous (1.63%). Pyrazines were identified as the major volatile organic components including 2,5-dimethyl pyrazine (2.964 mg/kg), 2,3-dimethyl-5-ethyl pyrazine (0.157 mg/kg) and trimethyl pyrazine (1.152 mg/kg), and 2-methylbutanal and 3-methylbutanal were identified at 3.015 mg/kg and 4.647 mg/kg respectively.

In Korean sesame oil the volatile organic components were consisted of 16 N-compounds, 5 alcohols, 11 aldehydes, 1 hydrocarbons, 2 S-compounds, 2 esters, 2 ketones and 3 miscellaneous. The relative area obtained for each functional group was N-compounds (45.23%), alcohols (32.67%), aldehydes (12.96%), hydrocarbons (1.25%), S-compounds (0.63%), esters (4.47%), ketones (0,78%) and miscellaneous (2.01%).

The yield of volatile organic components from Indian, Sudanese, Chinese and Korean sesame oils was 30.748, 37.759, 21.766 and 49.196 mg/kg, respectively.

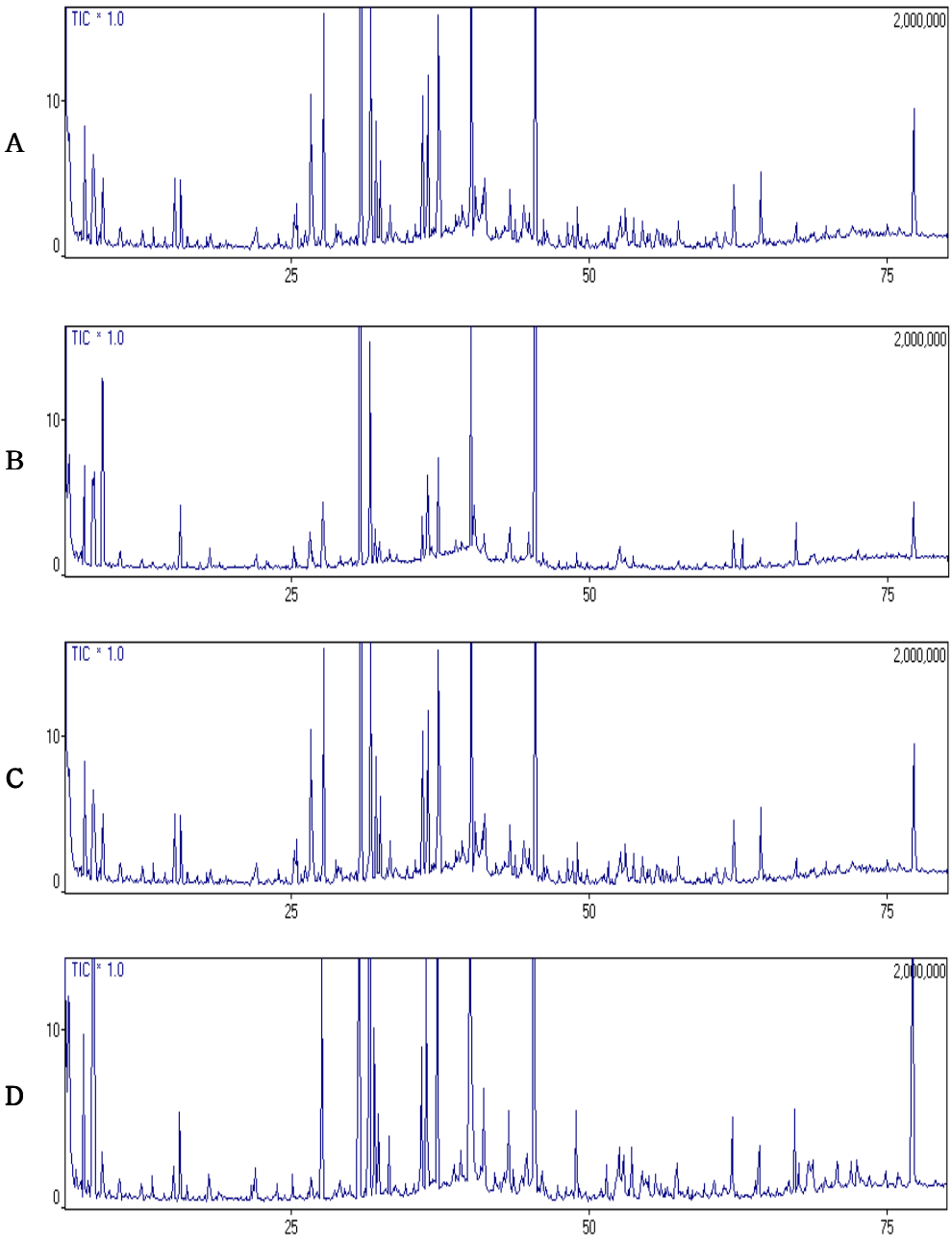

Fig. 18. GC/MS chromatograms of volatile flavor components in sesame oils. A: India, B: Sudan, C: China, D: Korea.

Table 20. Volatile components identified from sesame oils

No.	RT[1])	RI[2])	Compound Name	MF[3])	MW[4])	mg/kg			
						S-1[5])	S-2	S-3	S-4
1	6.138	808	2-Methyl propanal	C_4H_8O	72	-	0.570	0.073	0.177
2	6.394	822	Ethyl formate	$C_3H_6O_2$	74	0.307	0.904	0.269	0.904
5	7.421	874	Butanal	C_4H_8O	72	0.047	0.037	0.053	0.062
6	7.688	886	Ethyl acetate	$C_4H_8O_2$	88	0.771	0.986	0.505	1.072
7	8.381	913	2-Methylbutanal	$C_5H_{10}O$	86	0.487	3.015	0.427	1.849
8	8.508	917	3-Methylbutanal	$C_5H_{10}O$	86	0.365	4.647	0.466	1.612
9	8.932	930	3-Methyl-2-butanone	$C_5H_{10}O$	86	0.049	-	-	-
10	9.217	938	Ethanol	C_2H_6O	46	0.344	0.349	0.921	0.234
11	10.696	979	Pentanal	$C_5H_{10}O$	86	0.146	-	0.121	0.172
12	12.555	1022	Thiophene	C_4H_4S	84	0.153	-	-	-
13	14.367	1058	2,3-Pentanedione	$C_5H_8O_2$	100	-	0.049	-	-
14	15.23	1074	Dimethyl difulfide	$C_2H_6S_2$	94	0.407	0.134	0.055	0.218
15	15.743	1083	Hexanal	$C_6H_{12}O$	100	0.363	0.336	0.336	0.468
16	17.133	1106	Sabinene	$C_{10}H_{16}$	136	0.054	-	-	-
17	17.908	1120	2-Methyl thiophene	C_5H_6S	98	0.067	-	-	-
18	18.113	1123	3-Methyl hexanal	$C_7H_{14}O$	114	-	-	-	0.234
19	21.967	1183	2-Heptanone	$C_7H_{14}O$	114	0.061	-	-	0.102
20	22.139	1186	Pyridine	C_5H_5N	79	0.116	-	0.070	0.163
21	23.833	1211	Pyrazine	$C_4H_4N_2$	80	-	-	-	0.120
22	25.25	1233	2-Pentyl furan	$C_9H_{14}O$	138	0.180	0.125	0.109	0.160

[1)]Retention Time, [2)]Retention Index, [3)]Molecular Formula, [4)]Molecular Weight, [5)]S-1: India, S-2: China, S-3: Sudan, S-4: Korea.

Table 20. Continued

No.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg			
						S-1[5)]	S-2	S-3	S-4
23	25.481	1237	(*E*)-β-Ocimene	$C_{10}H_{16}$	136	0.222	-	0.061	-
24	26.621	1254	(*Z*)-β-Ocimene	$C_{10}H_{16}$	136	0.880	-	0.215	-
25	26.826	1256	Pentanol	$C_5H_{12}O$	88	0.194	-	0.098	0.218
26	27.715	1269	Methyl pyrazine	$C_5H_6N_2$	94	1.514	0.644	0.385	1.753
28	28.771	1284	4-Methyl thiazole	C_4H_5NS	99	0.125	-	-	0.062
29	28.979	1286	2-Octanone	$C_8H_{16}O$	128	0.064	-	-	-
I.S.	*30.87*	*1314*	*Butylbenzene*	*$C_{10}H_{14}$*	*134*	-	-	-	-
30	31.686	1326	2,5-Dimethyl pyrazine	$C_6H_8N_2$	108	2.955	2.964	1.801	4.932
31	32.110	1333	2,6-Dimethyl pyrazine	$C_6H_8N_2$	108	0.772	0.532	0.222	0.987
32	32.465	1338	Ethyl pyrazine	$C_6H_8N_2$	108	0.550	0.212	0.128	0.475
33	33.327	1351	2,3-Dimethyl pyrazine	$C_6H_8N_2$	108	0.248	0.157	0.082	0.360
34	36.053	1389	2-Ethyl-5-methyl pyrazine	$C_7H_{10}N_2$	122	0.918	0.368	0.274	0.977
35	36.471	1395	2-Ethyl-6-methyl pyrazine	$C_7H_{10}N_2$	122	1.164	0.932	0.667	1.741
36	37.383	1409	Trimethyl pyrazine	$C_7H_{10}N_2$	122	1.652	1.152	0.086	2.584
37	38.841	1432	(*E*)-2-Octenal	$C_8H_{14}O$	126	0.101	-	-	0.103
38	39.075	1436	2-Furfurylmethanethiol	C_5H_6OS	114	0.136	-	-	-
39	39.381	1440	3-Ethyl-2,5-dimethyl pyrazine	$C_8H_{12}N_2$	136	0.182	-	-	0.212
40	40.136	1452	2,6-Dimethyl-3-ethyl pyrazine	$C_8H_{12}N_2$	136	2.803	1.940	1.803	3.843
41	40.408	1456	Acetic acid	$C_2H_4O_2$	60	0.592	0.293	0.272	0.551
42	41.026	1465	Furfural	$C_5H_4O_2$	96	0.289	-	-	-

[1)]Retention Time, [2)]Retention Index, [3)]Molecular Formula, [4)]Molecular Weight, [5)]S-1: India, S-2: China, S-3: Sudan, S-4: Korea.

Table 20. Continued

No.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg			
						S-1[5)]	S-2	S-3	S-4
43	41.254	1469	2,6-Diethyl pyrazine	$C_8H_{12}N_2$	136	0.431	0.244	0.214	0.637
44	43.391	1499	3,5-Diethyl-2-methyl pyrazine	$C_9H_{14}N_2$	150	0.536	0.432	0.386	0.747
45	43.813	1506	2-Acetyl furan	$C_6H_6O_2$	110	0.171	-	-	0.178
46	44.536	1518	1H-Pyrrole	C_4H_5NS	67	0.265	-	-	-
47	44.966	1525	Benzaldehyde	C_7H_6O	106	0.189	0.272	0.217	0.149
48	45.502	1534	2-Ethoxypropanol	$C_5H_{12}O_2$	104	6.433	12.129	9.364	10.853
49	46.204	1545	2-Allyl-5-methyl pyrazine	$C_8H_{10}N_2$	134	0.164	-	0.115	-
50	48.218	1575	5-Methylfurfural	$C_6H_6O_2$	110	0.237	-	-	-
51	48.681	1582	2-Pentylpiridine	$C_{10}H_{15}N$	149	0.151	-	-	-
52	49.045	1588	Bergamotene	$C_{15}H_{24}$	204	0.252	0.382	0.100	0.553
53	51.611	1630	2-Methyl-3-propenyl pyrazine	$C_8H_{10}N_2$	134	0.187	-	-	-
54	53.071	1654	Acetophenone	C_8H_8O	120	0.255	-	-	0.242
55	53.751	1665	Furfuryl alcohol	$C_5H_6O_2$	98	0.208	-	-	-
56	53.606	1663	2,5-Dimethyl-3-isopentyl pyrazine	$C_{11}H_{18}N_2$	178	-	-	-	0.353
57	62.153	1816	*(E,E)*-2,4-Decadienal	$C_{10}H_{16}O$	152	0.342	0.168	0.207	0.411
58	62.842	1832	4-Allylmethoxybenzene	$C_{10}H_{12}O$	148	-	-	0.197	-
59	64.422	1867	Guaiacol	$C_7H_8O_2$	124	0.454	-	-	0.322
60	67.398	1941	2-Phenyl-2-butenal	$C_{10}H_{10}O$	146	0.107	0.950	0.273	0.489
61	70.877	2036	3,4-Dimethoxystyrene	$C_{10}H_{12}O_2$	164	-	0.197	-	-
62	68.822	1980	2-Acethylpyrrole	C_6H_7NO	109	-	-	-	0.106
63	77.284	2208	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	150	1.025	2.639	0.474	2.811
			Total			30.748	37.759	21.766	37.759

[1)]Retention Time, [2)]Retention Index, [3)]Molecular Formula, [4)]Molecular Weight, [5)]S-1: India, S-2: China, S-3: Sudan, S-4: Korea.

Table 21. Relative content of functional groups in identified volatile components from sesame oils

Functional group	India		China		Sudan		Korea	
	No.	Area %	No.	Area %	No.	Area %	No.	Area %
Alcohols	7	29.26	3	40.03	4	49.88	5	32.67
Aldehydes	11	7.80	8	26.48	9	9.99	11	12.96
Esters	2	3.51	2	5.01	2	3.56	2	4.47
Hydrocarbons	4	4.58	1	1.01	3	1.73	1	1.25
Ketones	4	1.40	1	0.13	-	-	2	0.78
N-Compounds	16	46.65	11	25.36	13	31.94	16	45.23
S-Compounds	6	3.74	1	0.35	1	0.25	2	0.63
Miscellaneous	3	3.06	3	1.63	3	2.65	3	2.01
Total	53	100	30	100	35	100	42	100

b. Analysis of volatile organic components of corn oil, soybean oil and rapeseed oil

The volatile organic components of corn oil, soybean oil and rapeseed oil were extracted using SDE and identified by GC/MS. The GC/MS chromatograms of volatile organic components and their percentage peak areas are shown in Fig. 19 and Table 22, respectively. The classification of volatile organic components by functional groups is shown in Table 23.

34 components were identified in corn oil (corn oil I) produced by H corporation, which consisted of 15 hydrocarbons, 10 aldehydes, 3 esters, 3 alcohols and 3 miscellaneous. The relative area obtained for each functional group was hydrocarbons (11.55%), aldehyde (9.49%), esters (5.90%), alcohols (5.86%) and miscellaneous (67.40%). 2-ethoxypropanol (67.06%) was the major component, which may be due to the lipid oxidation. 23 components were identified in corn oil (corn oil II) produced by B corporation, which consisted of 13 hydrocarbons, 6 aldehydes, 2 esters, 1 alcohol and 1 miscellaneous. Corn oil (corn oil III) produced by D corporation contained volatile components including 12 hydrocarbons, 9 aldehydes, 2 esters, 1 alcohol, 1 acid and 1 miscellaneous. The major volatile organic components were (*E,E*)-2,4-decadienal(8.90%), (Z)-heptenal (4.94%) and (*E*)-2-decenal (1.97%),.

31 volatile organic components were identified in soybean oil, which consisted of 11 aldehydes, 2 esters, 9 hydrocarbons, 5 alcohols, 2 ketones and 2 miscellaneous. The major component was (E)-2-heptenal accounting for 18.22%.

31 volatile organic components were identified in rapeseed oil, which consisted of 13 aldehydes (52.37%), 5 hydrocarbons (7.80%), 3 alcohols (7.18%), 2

esters (12.81%), 2 ketones (5.76%) and 1 miscellaneous (14.08%). The major components were (*E*) 2-heptenal, (*E,Z*)-2,4-decadienal and (*E,E*)-2,4-decadiena.

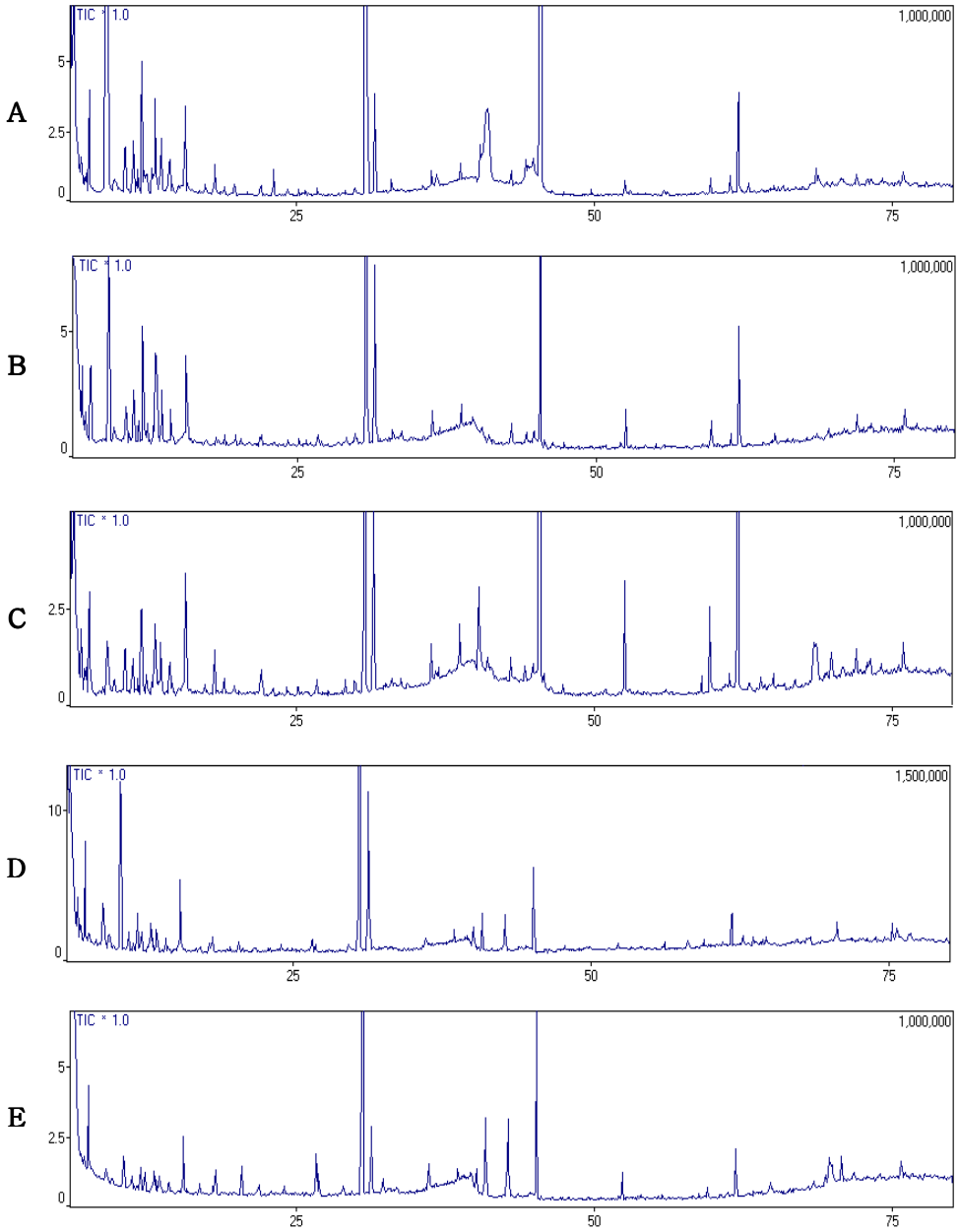

Fig. 19. GC/MS chromatograms of volatile organic components in vegetable oils. A: Corn oil I, B: Corn oil II, C: Corn oil III, D: Soybean oil, E: Rapeseed oil

Table 22. Volatile components identified from corn, soybean and rapeseed oils

No.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg				
						C-1[5)]	C-2	C-3	S	R
1	6.394	822	Ethyl formate	$C_3H_6O_2$	74	0.397	0.061	0.294	0.372	0.194
2	6.979	853	4-Octene	C_8H_{16}	112	0.048	0.095	0.102	0.126	-
3	7.239	865	2-Octene	C_8H_{16}	112	0.022	0.034	0.053	0.047	-
4	7.421	874	Butanal	C_4H_8O	72	0.034	-	0.039	-	-
5	7.688	886	Ethyl acetate	$C_4H_8O_2$	88	0.256	0.149	0.290	0.385	0.210
6	9.217	938	Ethanol	C_2H_6O	46	0.646	0.677	0.113	0.139	-
7	9.664	951	2-Methyl-1,3-dioxolane	$C_4H_8O_2$	88	0.022	-	-	0.054	-
8	9.912	958	2,6-Dimethyloctane	$C_{10}H_{22}$	142	0.020	-	-	0.036	-
9	10.696	979	Pentanal	$C_5H_{10}O$	86	0.148	0.076	0.116	0.725	0.082
10	11.312	994	2,2-Dimethyloctane	$C_{10}H_{20}$	142	0.119	0.087	0.073	0.057	0.027
11	11.525	999	Decane	$C_{10}H_{22}$	142	0.042	-	-	0.018	-
12	11.714	1003	Unknown	-	-	0.038	0.083	-	-	-
13	12.046	1011	2,6-Dimethylnonane	$C_{11}H_{24}$	156	0.330	0.211	0.194	0.161	0.077
14	12.273	1016	Unknown	-	-	0.080	0.049	-	-	
15	12.427	1019	Unknown	-	-	-	0.041	0.037	-	0.059
16	12.920	1030	Unknown	-	-	0.060	0.024	-	-	-
17	13.038	1032	Unknown	-	-	0.029	0.021	-	-	-
18	13.160	1034	2,9-Dimethyldecane	$C_{12}H_{26}$	170	0.250	0.171	0.141	0.128	0.051
19	13.247	1036	2-Butenal	C_4H_6O	70	-	-	-	0.078	0.030
20	13.358	1039	Unknown	-	-	0.068	0.049	0.043	-	-

[1)]Retention Time, [2)]Retention Index, [3)]Molecular Formula, [4)]Molecular Weight, [5)]C-1:Corn oil A, C-2: Corn oil B, C-3: Corn oil C, S: Soybean oil, R: Rapeseed oil.

Table 22. Continued

No.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg				
						C-1[5)]	C-2	C-3	S	R
21	13.658	1044	3-Methyldodecane	$C_{13}H_{28}$	184	0.178	0.083	0.104	0.066	0.032
22	14.396	1059	Unknown	-	-	-	-	0.054	0.052	-
23	14.398	1059	3-Methyl-5-propyl-nonane	$C_{13}H_{28}$	184	0.082	0.058	-	-	-
24	15.743	1083	Hexanal	$C_6H_{12}O$	100	0.239	0.149	0.279	0.334	0.175
25	17.382	1110	3-Pentanol	$C_5H_{12}O$	88	0.016	-	-	-	-
26	18.148	1124	3-Methyl hexanal	$C_7H_{14}O$	114	-	-	0.109	-	-
27	18.178	1124	2-Pentanol	$C_5H_{12}O$	88	0.078	-	-	0.032	0.051
28	18.238	1125	(*E*)-2-Pentenal	C_5H_8O	84	-	-	-	0.063	0.089
29	20.427	1161	1-Penten-3-ol	$C_5H_{10}O$	84	-	-	-	-	0.092
30	22.053	1184	Heptanal	$C_7H_{14}O$	114	-	-	0.046	0.068	0.042
31	23.099	1199	Dodecane	$C_{12}H_{26}$	170	0.066	-	-	-	-
32	24.042	1214	(*E*)-2-Hexenal	$C_6H_{12}O$	100	-	-	-	0.051	-
33	25.250	1233	2-Pentyl furan	$C_9H_{14}O$	138	0.022	-	-	-	-
34	26.558	1253	Pentanol	$C_5H_{12}O$	88	-	-	-	0.044	-
35	26.656	1254	1-Cyclohexylmethylketone	$C_8H_{12}O$	124	-	-	-	0.064	0.117
36	26.892	1257	Bicyclo[3.2.1]octan-3-one	$C_8H_{12}O$	124	-	-	-	0.039	0.065
37	28.942	1286	Octanal	$C_8H_{16}O$	128	-	-	-	-	0.036
I.S.	30.870	1314	Butylbenzene	$C_{10}H_{14}$	134	-	-	-	-	-
38	31.550	1324	(*E*)-2-Heptenal	$C_7H_{12}O$	112	0.287	0.362	0.746	0.913	0.242
39	36.364	1393	Nonanal	$C_9H_{18}O$	142	0.042	-	0.099	0.055	0.065
40	38.841	1432	(*E*)-2-Octenal	$C_8H_{14}O$	126	0.059	-	0.096	-	-

[1)]Retention Time, [2)]Retention Index, [3)]Molecular Formula, [4)]Molecular Weight, [5)]C-1:Corn oil A, C-2: Corn oil B, C-3: Corn oil C, S: Soybean oil, R: Rapeseed oil.

Table 22. Continued

No.	RT[1)]	RI[2)]	Compound Name	MF[3)]	MW[4)]	mg/kg				
						C-1[5)]	C-2	C-3	S	R
41	40.136	1452	1-Octen-3-ol	$C_8H_{16}O$	128	-	-	-	0.130	0.082
42	40.408	1456	Acetic acid	$C_2H_4O_2$	60	-	-	0.342	-	-
43	40.871	1463	*(E,Z)*-2,4-Heptadienal	$C_7H_{10}O$	110	-	-	-	0.233	0.309
44	40.979	1465	Octyl acetate	$C_{10}H_{20}O_2$	136	0.092	-	-	-	-
45	42.779	1491	*(E,E)*-2,4-Heptadienal	$C_7H_{10}O$	110	-	-	-	0.224	0.322
46	43.813	1506	2-Acetyl furan	$C_6H_6O_2$	110	-	-	15.113	-	-
47	44.966	1525	Benzaldehyde	C_7H_6O	106	0.001	-	0.047	-	-
48	45.502	1534	2-Ethoxypropanol	$C_5H_{12}O_2$	104	8.463	0.421	9.829	0.019	0.444
49	52.608	1646	*(E)*-2-Decenal	$C_{10}H_{18}O$	154	0.046	0.092	0.298	-	0.068
50	59.770	1770	*(E,Z)*-2,4-Decadienal	$C_{10}H_{16}O$	152	0.045	0.060	0.224	-	0.028
51	62.153	1816	*(E,E)*-2,4-Decadienal	$C_{10}H_{16}O$	152	0.297	0.250	1.345	0.263	0.163
Total						12.620	8.257	15.113	5.010	3.153

[1)]Retention Time, [2)]Retention Index, [3)]Molecular Formula, [4)]Molecular Weight, [5)]C-1:Corn oil A, C-2: Corn oil B, C-3: Corn oil C, S: Soybean oil, R: Rapeseed oil.

Table 23. Relative content of functional groups in identified volatile components from corn, soybean and rapeseed oils

Functional group	Corn oil A		Corn oil B		Corn oil C		Soybean oil		Rapeseed oil	
	No.	Area %	No.	Area %	No.	Area %	No.	Area %	No.	Area %
Aldehydes	10	9.49	6	30.33	12	22.78	11	59.35	13	52.37
Ketones	-	-	-	-	-	-	2	2.05	2	5.76
Esters	3	5.90	2	6.44	2	3.87	2	15.11	2	12.81
Alcohols	3	5.86	1	20.78	1	0.75	5	8.25	3	7.18
Acids	-	-	-	-	1	2.26	-	-	-	-
Hydrocarbons	15	11.35	13	29.51	9	5.30	9	13.78	5	7.80
Miscellaneous	3	67.40	1	12.94	1	65.04	2	1.46	1	14.08
Total	34	100	23	100	26	100	31	100	26	100

c. Discrimination of adulteration of sesame oil by volatile organic componets

Volatile organic components were extracted from sesame oil from different countries and other commercially available oils (corn oil, soybean oil and rapeseed oil)..

Most of the volatile components of commercial oils appeared in the DB-WAX column during the time period of 10~20 minutes, while in case of sesame oil, most of the volatile components were detected during the time period of 25~45 min (Fig 20). During the above analysis, the same samplrs were applied to GC/MS. From above experimental results, what was concluded is that the compounds; 2,6-dimethylnonane and 2,9-dimethyldecane can be used as marker compounds for detecting adulterated sesame oil (Fig 21).

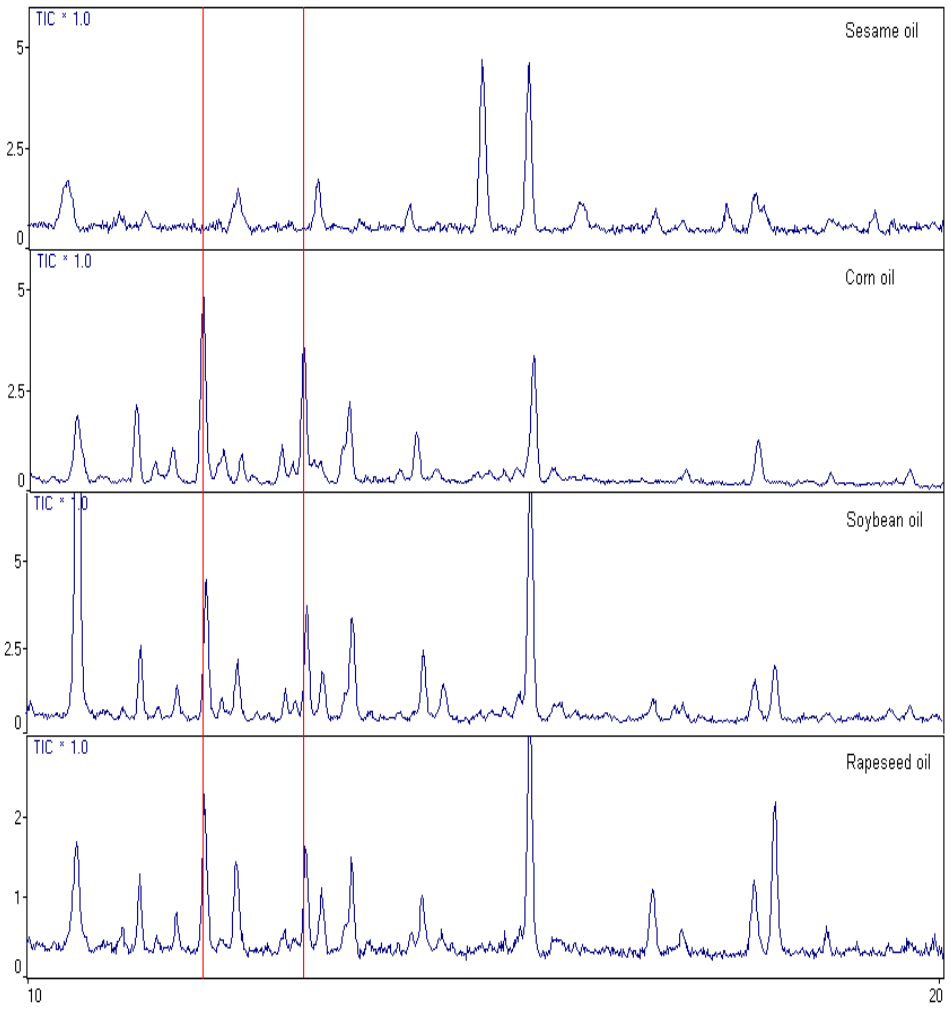

Fig. 20. Zoomed chromatograms of volatile organic components in sesame and other vegetable oil.

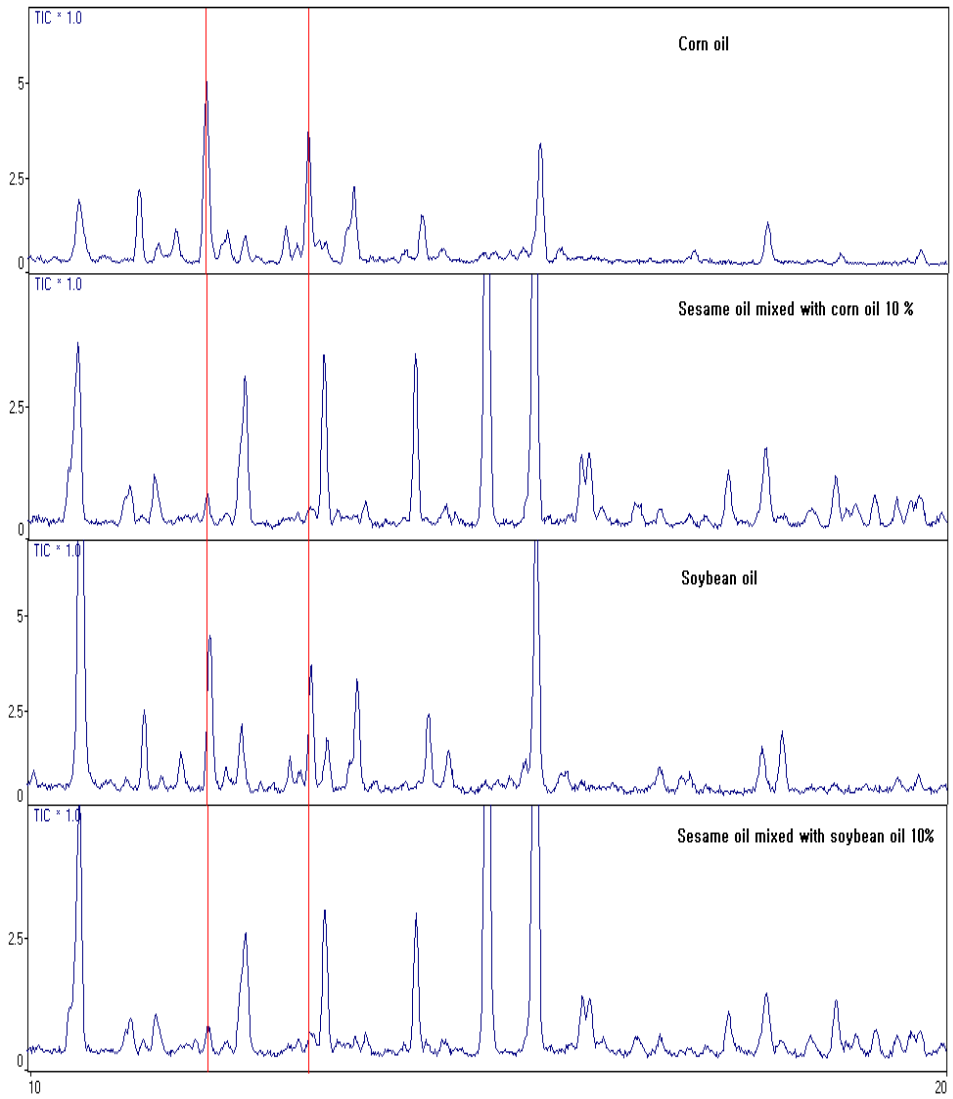

Fig. 21. Zoomed chromatograms of volatile organic components in adulterated sesame oils.

CONCLUSION

When sesame oil is adulterated with a corn oil, adulteration of corn oil more than 5% can be estimated by the ratio of $C_{16:0}\times C_{18:2}\times C_{18:3}/C_{18:0}+C_{18:1}$ fatty acids. The linear regression coefficient (r^2) was 0.987 for this determination, and a simple equation of y=0.0072x+1.2951 was fit to the data. Soybean oils cam be detected in sesame oil by content of linoleic acid and the ratio of $C_{18:1}/C_{18:2}$, and rapeseed oil can be detected by the fatty acid, and contents of linoleic and erucic acid and ratio the of $C_{18:2}/C_{18:1}$ fatty acids. Linoleic acid content of more than 0.5% that can be estimated corn, soybean and rapeseed oil as foreign oils, and if linoleic acid content was more than 1% can be used to estimate the percent of foreign soybean and rapeseed oils. Linoleic acid content beteween 0.5% and 1% can be detected by carbon isotope analysis. Analysis of sesamin content by HPLC was not applicable to detection of adulteration because various range of sesamin are present in sesame oils of defferent origin. NIR spectroscopy can be useful for discriminating the geographical origin of sesame oil but not for detection of adulterated sesame oil. Analysis of volatile organic compounds by GC/MS as adetection method for adulterated sesame oil may be useful because corn, soybean and rapeseed oil have characteristic compounds. In conclusion, corn, soybean and rapeseed oil contents of more than 10% (v/v) in adulterated sesame oil can be easily detected using the above methods.

요 약

참기름에 여타 식용유지를 첨가한 가짜참기름의 식품위생상 큰 문제를 일으키고 있어 가짜참기름의 식별을 위한 진위판별법을 개발하고자 하였다.

참기름은 직접 착유하여 사용하였으며, 참기름에 가짜 참기름 제조에 주로 이용되는 옥배유를 5, 10, 20, 30, 40, 50, 75 및 80%를 첨가하여, 대두유 및 채종유를 5, 10, 20, 40 및 80% 첨가하여 변조참기름을 제조한 뒤 GC 및 GC/MS 분석기기에 의한 지방산 조성 분석, HPLC 분석에 의한 sesamin 함량 분석, 탄소동위원소분석 및 NIR 분석법을 검토하였다. 또한, 참기름과 기타 식용유의 휘발성 유기성분을 GC/MS로 분석하여 비교하였다.

가짜참기름 제조 시 옥배유를 첨가했을 때, 5% 이상의 혼입율이 추정 가능하였다. 변조참기름의 지방산 분석을 통하여 유용한 지방산 비율은 $C_{16:0}\times C_{18:2}\times C_{18:3}/C_{18:0}+C_{18:1}$으로 혼입율이 증가함에 따라 직선상으로 증가하였으며, linear regression 상수 (r^2)는 0.987 이었고, y=0.0072x+1.2951의 관계식이 성립되었다. 대두유를 첨가했을 때에는, linoleic acid의 함량과 $C_{18:1}/C_{18:2}$의 비율로 5% 이상의 혼입율을 검출하였다. 유용한 지방산 비율은 대두유의 혼입율이 증가함에 따라 직선상으로 감소하였으며 (r^2=0.999) 상관관계식은 y=-0.0044x +0.8334이었다. 참기름에 혼입된 채종유는, lnoleic acid의 함량과 erucic acid의 검출로 확인 가능하였으며 혼입비율은 $C_{18:2}/C_{18:1}$의 비율을 이용하여 판별하였다. 상관관계식은 y=-0.0084+ 1.1528이었고 linear regression 상수 (r^2)는 0.992로 5%이상의 혼입비율을 판별할 수 있었다. 지방산 조성 분석에 의한 간편 방법 (1차 선별)으로는 linolenic acid의 함량 비교로 확인할 수 있으며, linolenic acid 0.5%이상의 경우 옥배유, 대두유, 채종유의 혼입을 추정할 수 있고 1.0% 이상의 경우 대두유와 채종유의 혼입을 추정할 수 있다.

Linolenic acid의 함량이 0.5～1.0% 사이로 분석되었을 경우, C^{13} isotope 분석으로 corn oil (C_4 plant)첨가를 확인할 수 있었다.

Sesamin 함량 분석에 의한 가짜참기름의 진위판별법으로는 참깨의 원산지에 따라 sesamin 함량의 범위가 다양하여 적용할 수 없으며, NIR 분석법으로는 참기름의 원산지 구별에는 유용하였으나 가짜참기름의 판별법으로는 유용하지 않았다. GC/MS에 의한 휘발성 유기성분의 분석으로 참기름에 존재하지 않는 휘발성 화합물이 옥배유, 대두유 및 채종유에서 공통적으로 확인되어 타 식용유의 첨가를 확인할 수 있었다. 결과적으로, 본 연구를 통해 옥배유, 대두유, 채종유의 혼합비율을 10%이상 검출 가능하였다.

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