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Fatty acid composition and characterisation of commercial vegetable oils with chemometric approaches

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Abstract

The fatty acid (FA) composition of 11 types of vegetable oils (n = 115) marketed in South Korea was investigated using GC-FID. Unique characterisation of FA profiles was observed in the vegetable oils. Coconut oil showed the highest content of saturated FA (SFA) (93.30%). The content of monounsaturated FA (MUFA) and polyunsaturated FA (PUFA) were highest in olive oil (76.44%) and perilla oil (80.14%). Rice bran oil (1.69) and olive oil (0.56) showed the ideal ratio of PUFA/SFA. Multivariate statistical techniques including principal component analysis (PCA), cluster analysis (CA), and linear discriminant analysis (LDA) were applied to the chromatographic data of FAs. The differences and similarities between the vegetable oils were clearly observed with PCA and CA. A dendrogram using Ward linkage showed that the vegetable oils were grouped into three clusters. The adulterated samples of sesame oil and perilla oil with cheaper oils such as corn oil and soybean oil could be sensitively detected by LDA even at a 2% mixing level. Stearic acid (Wilk's $\lambda = 0.632$) and palmitic acid (Wilk's $\lambda = 0.407$) showed the highest discriminant power for adulterated sesame oil and perilla oil, respectively.

Introduction

Edible fats and oils are the main sources of energy (9 calories/g) and essential nutrients for mankind (Ganesan *et al.,* 2018). In total, 95 - 98% of dietary vegetable oils are composed of triacylglycerol, which consists of a single unit of glycerol molecule and three fatty acids (FAs) (Lerma-Garcia *et al.,* 2011). FAs can generally be categorised into saturated FA (SFA), monounsaturated FA (MUFA) and polyunsaturated FA (PUFA) based on the presence and number of double bonds. The ratio of unsaturated to saturated FAs in dietary oils and fats is a major factor that influences human nutrition associated with plasmatic cholesterol and obesity (Kostik *et al.,* 2013). Generally, SFA, which have no double bonds, are known to increase the level of low-density lipoproteins, and are one of various factors that can increase the risk of coronary heart disease (CHD) (World Health Organization, 2008). Meanwhile, dietary MUFA and PUFA not only have beneficial effects on the blood lipid profile but also show the ability to decrease the risk of CHD (Metcalf *et al.,* 2007). PUFA including linoleic ($C_{18:2n-6}$) and α-linolenic ($C_{18:3n-3}$) are regarded as essential FAs that should be supplied through dietary food as they cannot be synthesised in our bodies (Dorni *et al.,* 2018).

The composition and content of FAs in dietary vegetable oils differ depending on their origins and thus influence their functional and physical properties (Lerma-Garcia *et al.,* 2011). The characteristics of FAs can be utilised to identify the botanical origin and intentional adulteration of vegetable oils (Li *et al.,* 2011; Galão *et al.,* 2014; Zhang *et al.,* 2014). Meanwhile, it has been reported that there are clear limitations to detecting the adulteration of vegetable oils with just analysing the composition of FAs due to the similarity of FA composition in some edible oils and the wide range of adulterated edible oils (El-Hamdy and El-Fizga, 1995; Li *et al.,* 2011).

Even if the adulteration of edible oils, which usually involves the mixing of expensive oils with cheaper oils, is not severely harmful to human health, it is related to economic motivation and consumer's right for buying "value-for-money" (Ulberth and Buchgraber, 2000). Much research has been conducted into effectively detecting the adulteration of edible oils such as adulterated olive oil and flaxseed oil, with a combination of analytical techniques and multivariate statistical approaches through characterising FA profiles or triacylglycerol (Ruiz-Samblás *et al.,* 2012; Monfreda *et al.,* 2014; Sun *et al.,* 2015; Jabeur *et al.,* 2017). In the case of sesame oil, which is largely consumed in Asian countries including South Korea and China, the

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problem of its adulteration has existed for a long time due to economic profits (Seo *et al.,* 2010). Several works have reported the detection techniques for adulterated sesame oil (Lee *et al.,* 2001; Park *et al.,* 2010; Peng *et al.,* 2015). Non-invasive analytical techniques including Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FT-IR) have been recently developed and applied to detect the adulteration of perilla oil with cheaper oils because of its high retail price (Kim *et al.,* 2018; Park *et al.,* 2019).

Chemometric methods have emerged as an efficient tool for the authentication and classification of edible vegetable oils; these usually utilise multivariate statistical and mathematical approaches to extract meaningful information from complicated analytical data (Brodnjak-Vončina *et al.,* 2005; Esteki *et al.,* 2018). Among the various tools of multivariate statistics, principal component analysis (PCA) and cluster analysis (CA) are commonly used to differentiate and group complex data; these can be very helpful to interpret food analytical data with visual representation (Giacomelli *et al.,* 2006; Chudzinska and Baralkiewicz, 2011; Kafaoğlu *et al.,* 2014). Linear discriminant analysis (LDA) has been frequently adopted for food chromatographic data to predict geographical origins and varieties, and to identify the adulteration of vegetable oils (Lee *et al.,* 1998; Lanteri *et al.,* 2002; Bosque-Sendra *et al.,* 2012; Callao and Ruisánchez, 2018).

The main objective of the present work was to evaluate the FA composition of 11 types of edible vegetable oils that are commonly consumed in the South Korean market via GC-FID analysis. Multivariate statistical techniques like PCA and CA were also performed to differentiate the characterisation of the vegetable oils' FA profiles. The LDA tool was applied to select FA variables showing the most discriminant power for authenticating sesame oil and perilla oil. The present work also observed the possibility of discriminating the adulterated samples of sesame oil and perilla oil that were blended with cheaper oils such as corn oil and soybean oil at the concentration range of 2 - 40% from authentic ones by LDA.

Materials and methods

Samples

A total of 115 vegetable oil samples were obtained from retail markets in Seoul, Korea which included local and imported products; canola oil (n = 11), coconut oil (n = 9), corn oil (n = 4), grapeseed oil (n = 7), flaxseed oil (n = 2), olive oil (n = 16), perilla oil (n = 25), rice bran oil (n = 2), sesame oil (n = 27), soybean oil (n = 7), and sunflower oil (n = 5). Korean markets sell a variety of sesame oil and perilla oil brands.

Chemicals and reagents

The analytical standard of FAs, fatty acids methyl ester (FAME) mix (C_4–C_{24}), was purchased from Supelco (Bellefonte, PA, USA). Analytical grade ethanol, methanol, chloroform, and iso-octane were purchased from Fisher Scientific Korea Ltd. (Seoul, Korea). The 14% boron trifluoride-methanol solution and undecanoic acid ($C_{11:0}$) methyl ester as an internal standard were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Sodium sulphate, sodium hydroxide, 0.01 M sodium thiosulfate solution, and Wijs reagent were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Distilled water was purified using the Milli-Q integral 5 system (Millipore Co., Billerica, MA, USA). A Standard Reference Material (SRM 3274-4) of perilla oil containing omega-3 and omega-6 FAs was used to validate the analytical method.

Esterification of FAs

The AOAC official method 969.33 (AOAC, 2000) was modified for the preparation of FAME. About 25 mg of the vegetable oil sample was accurately weighed in a screw-capped glass tube and 1 mL of the internal standard ($C_{11:0}$, 1 mg/mL iso-octane) was added. Then, 1.5 mL of 0.5 N of methanolic sodium hydroxide solution was added to the tube and it was mixed after blowing in nitrogen gas. The tube was heated in a dry block bath (MG-2200, Tokyo Rikakikai Co., Ltd., Japan) at 100°C for 5 min. After cooling, 2 mL of a 14% boron trifluoride-methanol solution was added to the tube, and it was immediately capped, vortexed, and heated at 100°C for 30 min. After cooling to 30 - 40°C, 1 mL of iso-octane solution was added to the tube and it was capped and mixed vigorously for 30 s. Afterward, 5 mL of saturated sodium chloride solution was added to the tube and it was agitated thoroughly. After cooling to room temperature, the layer of iso-octane separated from the aqueous layer was dehydrated with anhydrous sodium sulphate and was used as the final solution for analysis.

GC instrumental condition

FAME analysis was performed with a model of GC-2010 plus gas chromatography equipped with AOC-20i auto injector and flame ionisation detector (Shimadzu Corp., Japan). A SP-2560 fused silica capillary column (100 m × 0.25 mm × 0.2 μm) was used for separating FAs. The GC-FID operating conditions were as follows: injector temperature, 260°C; detector

temperature, 260°C; initial oven temperature, 140°C for 5 min, which was then raised at 3°C/min to 240°C and held at 240°C for 13 min. The total analysis time was 51.3 min. He was used as a carrier gas at a 0.7 mL/min flow rate. Hydrogen and air were kept at 40 and 400 mL/min flow rates, respectively. The injection volume was 1.0 µL, and the split ratio was 1:5.

Measurement of iodine value (IV)

The IV was measured by the Korean Food Standards Codex (MFDS, 2016) to determine the degree of unsaturation. Approximately 0.2 g of each oil sample was weighed in a 250 mL triangular flask with lid and then 20 mL of chloroform and 25 mL of Wijs (iodine monochloride) solution were added into the flask. Following incubation in the dark for 1 h, 20 mL of 1 N KI solution and 100 mL of water were added into the flask. Finally, the flask was titrated with 0.1 N sodium thiosulfate solution. A blank test was performed using the same procedures.

Multivariate statistical analysis

Multivariate statistical analyses including PCA, CA, and LDA were carried out using IBM SPSS Statistics 24.0 software (SPSS Inc.). PCA was performed to generate new variables, principal components (PCs), from five major FA variables (palmitic, stearic, oleic, linoleic, and linolenic). CA was conducted to show the organised clusters of the targeted vegetable oils. Their nearness in the multidimensional plot was presented in a dendrogram using Ward linkage. Two-group LDA was performed to find the coefficients of independent variables that maximised the difference in variance between the groups compared to the variance in the group. The adulterated samples of sesame oil and perilla oil were made with blending them with corn oil and soybean oil at different concentrations of 2, 5, 10, 20, 30, and 40%. Next, the LDA was applied to discriminate authentic sesame oil and perilla oil from the adulterated samples.

Results and discussion

FA composition of vegetable oils

A total of 115 samples from 11 types of edible vegetable oils collected from the local markets were analysed for characterising FA composition. The FA percent composition and the specific ratios of tested samples are shown in Table 1. The acquired peak areas from GC analysis were normalised using response factor, and the FA percent contents were calculated with the FAME conversion factor. The FA contents less than 0.1% were excluded from the analysis. As shown in Table 1, the number of items of sesame and perilla oils were significantly higher than the other oils, because those two oils have been used traditionally in Korea for a long time and produced by a large number of small-scale producers.

Recovery test was conducted for analytical quality assurance with SRM 3274-4. Major FA contents including palmitic ($C_{16:0}$), stearic ($C_{18:0}$), oleic ($C_{18:1}$), linoleic ($C_{18:2}$), and linolenic ($C_{18:3}$) acids were analysed with the same analytical procedures, and the recovery rates were obtained in the acceptable range of 82.8 - 100.2%.

The ten SFAs and seven USFAs were totally quantified in the tested oil samples, and it was confirmed that canola oil and rice bran oil comprised the largest number of FAs (12 kinds of FA). The coconut oil showed the highest percentage of SFA (93.30%) of all vegetable oils, and lauric acid ($C_{12:0}$), which is known as the indicator of quality control of coconut oil, was observed as the main FA (49.61%). This result is very similar to that of Dorni *et al.* (2018), in which coconut oil contained 49.57% lauric acid. Olive oil showed the highest content of MUFA (76.44%), followed by canola oil (60.58%). Olive oil was already reported in a previous study (Kostik *et al.,* 2013), which demonstrated that it had the highest proportion of MUFA of all vegetable oils (78.4%). It is well known that diet containing rich MUFA such as olive oil could lower the risk of CHD (Hu and Willett, 2002), and for that reason olive oil has been recognised as a healthy food because of its cardio protective effect. The average content of PUFA was the highest in the perilla oil (80.14%) within the range of 77.39 - 82.89% followed by flaxseed oil (73.45%) and grapeseed oil (70.44%). In contrast to that, the average SFA content of the perilla oil was the lowest (6.58%). Perilla oil yielded the highest proportion of linolenic acid (68.16%), and has been considered as a beneficial vegetable oil to human health, despite being easily oxidised due to high PUFA content (Longvah *et al.,* 2000). Meanwhile, grapeseed oil and sesame oil yielded the lowest proportion of linolenic acid, 0.30% and 0.32%, respectively. In the present work, the contents of linolenic acid of perilla oil were in the range of 65.57 - 70.75%, which are higher than that reported in a previous study (53.6 - 64.0%, Yoon and Noh, 2011). The variation of the content of linolenic acid can be explained by the study conducted by Were *et al.* (2006), in which the authors proposed that the content of linoleic acid and oleic acid in sesame oil might be affected by origin, genetic variance, refining process, and cultivation environment.

The ideal ratio of TPUFA/TSFA recommended by the WHO is 0.8 - 1.0 (WHO, 2008), and in the present work, the rice bran oil (1.69) and olive oil

Table 1. Fatty acids composition and specific ratios of commercial vegetable oils analysed by GC-FID.

	Fatty acids content (%, Mean ± SD)										
	Canola (*n* = 11)	**Coconut (*n* = 9)**	**Corn (*n* = 4)**	**Grapeseed (*n* = 7)**	**Flaxseed (*n* = 2)**	**Olive (*n* = 16)**	**Perilla (*n* = 25)**	**Rice bran (*n* = 2)**	**Sesame (*n* = 27)**	**Soybean (*n* = 7)**	**Sunflower (*n* = 5)**
$C_{6:0}$ (Caproic)	ND[a]	0.56 ± 0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND
$C_{8:0}$ (Caprylic)	ND	7.39 ± 0.46	ND	ND	ND	ND	ND	ND	ND	ND	ND
$C_{10:0}$ (Capric)	ND	6.02 ± 0.38	ND	ND	ND	ND	ND	ND	ND	ND	ND
$C_{12:0}$ (Lauric)	ND	49.61 ± 1.44	ND	ND	ND	ND	ND	ND	ND	ND	ND
$C_{14:0}$ (Myristic)	ND	18.44 ± 0.69	ND	ND	ND	ND	ND	0.31 ± 0.01	ND	ND	ND
$C_{16:0}$ (Palmitic)	4.12 ± 0.19	8.33 ± 0.69	10.85 ± 0.25	6.60 ± 0.32	4.54 ± 0.33	11.55 ± 1.31	4.94 ± 0.23	18.02 ± 0.41	8.64 ± 0.41	10.10 ± 0.30	5.83 ± 0.37
$C_{18:0}$ (Stearic)	1.81 ± 0.12	2.93 ± 0.17	1.74 ± 0.02	10.85 ± 0.25	3.32 ± 0.06	2.98 ± 0.59	1.56 ± 0.19	2.10 ± 0.02	5.14 ± 0.24	3.94 ± 0.30	3.24 ± 0.19
$C_{20:0}$ (Arachidic)	0.55 ± 0.21	ND	0.41 ± 0.01	0.16 ± 0.04	0.12 ± 0.02	0.37 ± 0.55	ND	0.79 ± 0.07	0.51 ± 0.04	0.31 ± 0.03	0.21 ± 0.01
$C_{22:0}$ (Behenic)	0.30 ± 0.05	ND	0.13 ± 0.01	0.11 ± 0.12	0.11 ± 0.01	0.10 ± 0.02	ND	0.27 ± 0.03	0.10 ± 0.02	0.34 ± 0.05	0.59 ± 0.08
$C_{24:0}$ (Lignoceric)	0.13 ± 0.03	ND	0.17 ± 0.01	ND	ND	ND	ND	0.40 ± 0.06	ND	0.11 ± 0.03	0.19 ± 0.03
$C_{16:1}$ (Palmitoleic)	0.17 ± 0.01	ND	ND	ND	ND	0.87 ± 0.23	ND	0.16 ± 0.00	ND	ND	ND
$C_{18:1}$ (Oleic)	59.08 ± 1.55	5.54 ± 0.79	29.48 ± 0.70	18.71 ± 2.04	18.20 ± 3.16	75.31 ± 3.50	13.11 ± 2.53	40.38 ± 0.68	39.06 ± 1.21	22.47 ± 1.45	26.28 ± 2.67
$C_{18:2n-6}$ (Linoleic)	22.14 ± 1.48	1.16 ± 0.48	55.80 ± 0.82	70.13 ± 2.31	16.60 ± 1.83	7.79 ± 2.42	11.98 ± 0.88	35.35 ± 1.09	45.95 ± 1.22	55.17 ± 1.00	62.97 ± 2.77
$C_{18:3n-6}$ (γ-Linolenic)	0.59 ± 0.29	ND	ND	ND	0.19 ± 0.00	ND	0.23 ± 0.04	0.20 ± 0.06	ND	0.53 ± 0.17	ND
$C_{18:3n-3}$ (α-Linolenic)	9.68 ± 0.75	ND	1.07 ± 0.12	0.30 ± 0.04	56.66 ± 1.09	0.72 ± 0.07	67.93 ± 2.55	1.47 ± 0.21	0.32 ± 0.03	6.51 ± 0.78	0.38 ± 0.48
$C_{20:1}$ (Eicosenoic)	1.19 ± 0.29	ND	0.20 ± 0.01	0.12 ± 0.02	0.12 ± 0.02	0.20 ± 0.05	0.16 ± 0.04	0.49 ± 0.03	0.13 ± 0.01	0.27 ± 0.15	0.15 ± 0.05
$C_{24:1}$ (Nervonic)	0.14 ± 0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TSFA[b]	7.01 ± 0.26	93.30 ± 1.26	13.38 ± 0.27	10.65 ± 0.48	8.23 ± 0.26	15.05 ± 1.01	6.58 ± 0.36	21.95 ± 0.54	14.45 ± 0.58	14.94 ± 0.45	10.16 ± 0.35
TMUFA[c]	60.58 ± 1.38	5.54 ± 0.79	29.75 ± 0.71	18.91 ± 2.05	18.32 ± 3.18	76.44 ± 3.25	13.28 ± 2.54	41.01 ± 0.71	39.28 ± 1.20	22.82 ± 1.46	26.50 ± 2.68
TPUFA[d]	32.41 ± 1.34	1.16 ± 0.48	56.87 ± 0.90	70.44 ± 2.26	73.45 ± 2.92	8.51 ± 2.42	80.14 ± 2.75	37.02 ± 1.25	46.27 ± 1.24	62.22 ± 1.56	63.34 ± 2.71
TPUFA/TSFA	4.63	0.01	4.25	6.63	8.93	0.56	12.23	1.69	3.21	4.16	6.24
Omega-6	22.73 ± 1.55	1.16 ± 0.48	55.80 ± 0.82	70.14 ± 2.30	16.79 ± 1.83	7.79 ± 2.42	12.21 ± 0.90	35.55 ± 1.04	45.95 ± 1.22	55.70 ± 0.95	62.97 ± 2.77
Omega-3	9.68 ± 0.75	ND	1.07 ± 0.12	0.30 ± 0.04	56.66 ± 1.09	0.72 ± 0.07	67.93 ± 2.55	1.47 ± 0.21	0.32 ± 0.03	6.51 ± 0.78	0.38 ± 0.48
Omega-6/Omega-3	2.37	-	52.57	235.32	0.30	10.95	0.18	24.45	144.10	8.65	594.71

[a]ND: not detected; [b]TSFA: total saturated fatty acids; [c]TMUFA: total monounsaturated fatty acids; [d]TPUFA: total polyunsaturated fatty acids. The content of fatty acids which were not larger than 0.1% (w/w) was omitted from the Table.

(0.56) yielded values closest to that. On the other hand, the perilla oil (12.23) and flaxseed oil (8.93) yielded the highest TPUFA/TSFA ratios. It is generally known that the high ratio of omega-6/omega-3 FAs in the diet can increase the incidence of many diseases, such as cardiovascular diseases, cancers, and inflammatory diseases (Simopoulos, 2002). The WHO recommends a consumption ratio of omega-6/omega-3 FAs of 5 - 10, whereas the ratio of the modern western diet is 15.0 - 16.7 owing to the high consumption of omega-6 FAs. The soybean oil and olive oil showed similar values, 8.65 and 10.95, respectively. In contrast, the sunflower oil (594.71) showed the highest ratio, followed by the grapeseed oil (235.32) and sesame oil (144.10).

Principal component analysis (PCA) and cluster analysis (CA)

PCA was carried out in order to establish and visualise the correlations of five major FA ($C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$) variables acquired from the FA analysis of 11 types of vegetable oils. Generally, PCA is used to generate new reduced variables, principal components (PCs), which can represent most variables from the original data (Lee *et al.,* 1998). The PCA was conducted for identifying the degree of similarity and difference of vegetable oils with their five major FA components. The correlation of variables in the present work was significant at $p < 0.05$, and the Kaiser-Meyer-Olkin (KMO) test indicated sampling adequacy was suited for factor analysis, with 0.655. Figure 1 shows the score and loading plot of PCA of the first two PCs which cumulatively accounted for 76.87% of the total variance, and it was confirmed in the score graph that the eigenvalues of these two PCs were higher than 1.0. Unlike other FAs, linolenic acid ($C_{18:3}$) only showed negative loading value on the plane of PC1 and PC2 in the loading plot. As shown in Figure 1, the 2-dimensional score plot of PCA of the first two PCs extracted from correlation matrix demonstrated that the distinct clusters of 11 vegetable oils were formed based on their different five major FAs composition. Li *et al.* (2011) suggested that corn and sesame oils cannot be distinguished in 3-dimensional PCA score plot owing to their similar FA compositions. Meanwhile, the positional difference between the two oils could be identified in the present work despite the very similarity of their FA composition. This similarity is the reason why adulterated sesame oil has been intentionally made with the addition of corn oil by unscrupulous food manufacturers.

The dendrogram using Ward linkage produced by CA is shown in Figure 2. The dendrogram clearly shows the clusters of vegetable oils having similar FA profiles. With the rescaled distance of 5 - 20, the vegetable oils were grouped in three clusters (group 1: sesame, soybean, corn, grapeseed, and sunflower oils; group 2: coconut, canola, perilla, and flaxseed oils; and group 3: olive and rice bran oils). It could be confirmed that these results show similar tendency, like the PCA plot. Looking at the ratio of TPUFA/TSFA of each group, group 1 showed a range of 3.21 - 6.63, while group 3 showed the lower value of 0.56 - 1.69. In the case of group 2, the ratio of TPUFA/TSFA was much higher than the other

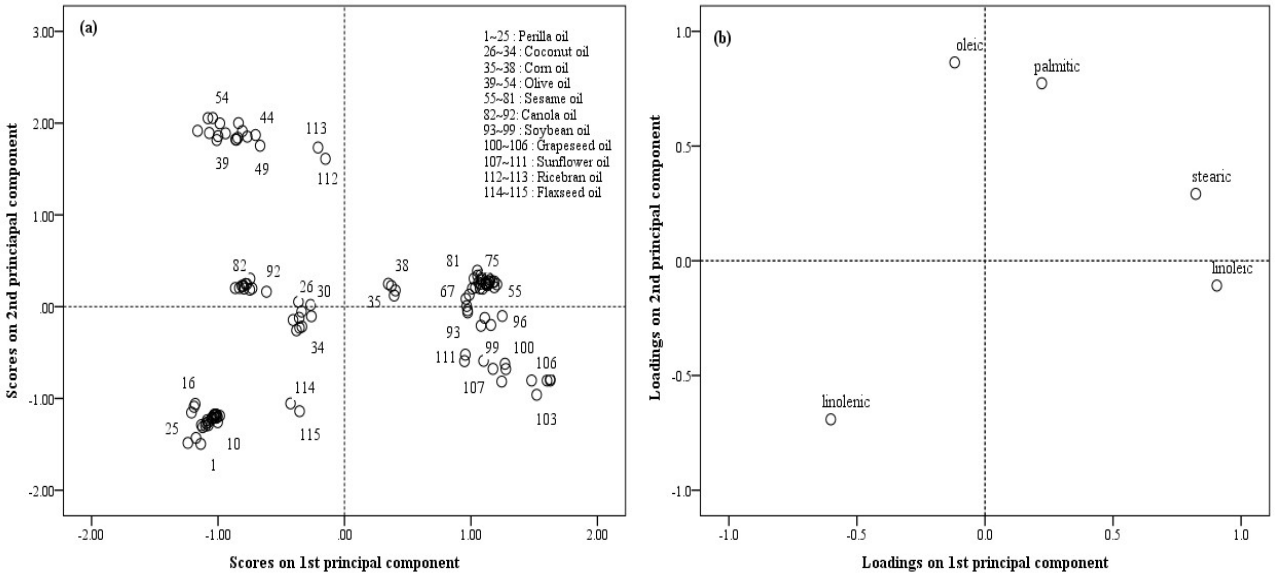

Figure 1. Principal component scores (a) and loadings (b) plot for the fatty acids of commercial vegetable oils.

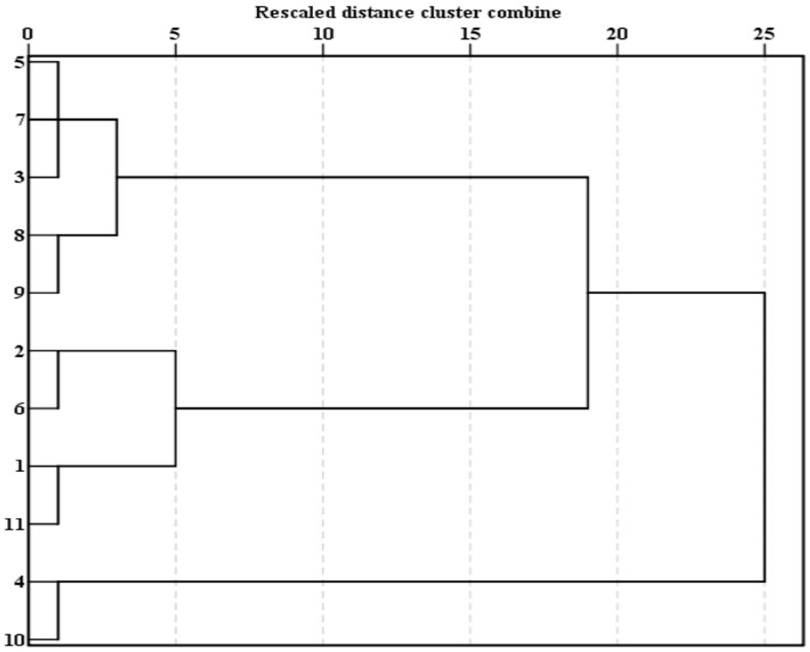

Figure 2. Dendrogram of cluster analysis using Ward linkage for commercial vegetable oils.

groups, at 8.93 - 12.23, with the exception of canola and coconut oils. With the PCA and CA, the similarities, and differences of vegetable oils based on the FA composition could be visualised and interpreted in a statistical graph. In addition, the results of PCA and CA provided the appropriate information for assessing the quality and authenticity of vegetable oils.

Linear discriminant analysis (LDA) for adulterated oils

The accurate detection technique for adulterated oils was suggested by combining chromatographic FA analysis with linear discriminant analysis (LDA). The adulterated samples of sesame oils and perilla oils were made with the addition of corn oil and soybean oil in the different percentages of 2, 5, 10, 20, 30, and 40% in order to observe the changes of five major FAs composition and iodine value. Table 2 shows the major FA composition and iodine values of the blended oils. As the percentage of added corn oil increased in the adulterated sesame oil, the content of TSFA slightly decreased from 15.05 to 14.23%, but the content of TPUFA increased from 44.99 to 49.16%. Park *et al.* (2010) proposed that the comparison of relative ratios (e.g. linoleic acid/stearic acid, etc.) from FA contents could be a useful tool to distinguish the adulterated sesame oil blended with soybean oil. Although the difference of relative ratios was somewhat effective to screen the adulterated sesame oils, there are limitations considering the FA composition of sesame oils varying by their origin and culture region. As means for inspecting the incorporation of heterogeneous oil into sesame oil, the linolenic acid content (less than 0.5%) and iodine value (103 - 118) have been set as quality indicators in the Food Standards Codex by the Korean Food and Drug Administration (KFDA). As shown in Table 2, it was confirmed that the linolenic acid content of the adulterated sesame oils met the specification standard when the addition of corn oil into sesame oil was less than 20%. In other words, there is no way to check the adulteration of sesame oil if corn oil was added at 20% or less. The iodine values of the adulterated sesame oils were in the range of 110.3 - 115.3, which conformed to the specification standard of authentic sesame oil. The values were very similar to the previous results reported by Joo *et al.* (2017), in which they suggested that the iodine values of adulterated sesame oils blended with corn oil (5 - 25%) were in the range of 107.5 - 109.9. Through these results, even if a large amount of vegetable oils having similar unsaturation were blended with sesame oil, it was difficult to distinguish the adulteration of sesame oil by only measuring the iodine value.

In the case of perilla oil, it is stated by the KFDA that the iodine value (160 - 209) is the unique quality parameter for inspecting the adulteration of perilla oil. As shown in Table 2, the content of linoleic acid apparently increased as the addition of soybean oil into perilla oil increased, while the content of linolenic acid dramatically decreased. Meanwhile, all the iodine values were measured in

Table 2. Major fatty acids composition, relative ratios, and iodine values of the blended oil.

Fatty acids (%FA)	% of mixing corn oil with sesame oil							% of mixing soybean oil with perilla oil						
	0	**2**	**5**	**10**	**20**	**30**	**40**	**0**	**2**	**5**	**10**	**20**	**30**	**40**
Palmitic ($C_{16:0}$)	8.95 ± 0.38[a]	8.96 ±0.35	9.03 ± 0.31	9.12 ± 0.36	9.26 ± 0.32	9.41 ± 0.27	9.56 ± 0.30	5.16 ± 0.18	5.30 ± 0.15	5.40 ± 0.14	5.56 ± 0.15	6.03 ± 0.18	6.46 ± 0.17	6.90 ± 0.19
Stearic ($C_{18:0}$)	5.18 ± 0.21	5.11 ± 0.15	5.01 ± 0.16	4.84 ± 0.15	4.49 ± 0.16	4.14 ± 0.19	3.80 ± 0.14	1.46 ± 0.15	1.48 ± 0.11	1.52 ± 0.12	1.63 ± 0.13	1.87 ± 0.15	2.13 ± 0.14	2.35 ± 0.13
Oleic ($C_{18:1}$)	39.76 ± 1.03	39.64 ± 0.64	39.35 ± 0.58	39.04 ± 0.54	38.00 ± 0.62	37.30 ± 0.52	36.39 ± 0.65	15.55 ± 1.21	15.64 ± 1.06	15.88 ± 1.12	16.26 ± 1.24	16.79 ± 1.22	17.30 ± 1.31	17.89 ± 1.33
Linoleic ($C_{18:2}$)	44.70 ± 1.15	44.92 ± 0.57	45.22 ± 0.55	45.55 ± 0.61	46.66 ± 0.63	47.57 ± 0.58	48.57 ± 0.68	11.22 ± 0.51	12.06 ± 0.47	13.25 ± 0.42	15.36 ± 0.53	19.62 ± 0.61	23.88 ± 0.72	28.35 ± 0.75
Linolenic ($C_{18:3}$)	0.29 ± 0.03	0.31 ± 0.02	0.33 ±0.03	0.37 ± 0.03	0.44 ± 0.04	0.52 ± 0.04	0.59 ± 0.05	66.20 ± 1.43	65.11 ± 1.28	63.53 ± 1.41	60.74 ± 1.44	55.15 ± 1.37	49.61 ± 1.26	43.90 ± 1.22
TSFA[b]	15.05	14.92	14.89	14.83	14.68	14.41	14.23	6.73	6.88	7.01	7.29	8.02	8.75	9.39
TPUFA[c]	44.99	45.23	45.55	45.92	47.10	48.08	49.16	77.57	77.33	76.94	76.29	74.99	73.71	72.47
TPUFA/TSFA	2.99	3.03	3.06	3.10	3.21	3.34	3.45	11.52	11.24	10.97	10.46	9.35	8.43	7.72
Iodine value	110.1 ± 0.9	110.3 ± 0.9	110.2 ± 0.8	109.8 ± 1.0	110.0 ± 0.9	114.8 ± 0.7	115.3 ± 0.8	185.8 ± 4.4	181.0 ± 2.0	180.9 ± 1.1	178.4 ± 2.8	175.0 ± 3.1	167.2 ± 2.2	162.7 ± 2.5

[a]: all experiments were triplicated and expressed as mean ± SD; [b]TSFA: total saturated fatty acids; [c]TPUFA: total polyunsaturated fatty acids.

the range of 162.7 - 181.0, regardless of the amount of soybean oil added, which was within the standard specification. It was also confirmed that when blended vegetable oils had a similar degree of unsaturation, it was impossible to detect the presence of heterogeneous oil in the perilla oil by just measuring the iodine value.

To solve these limits for distinguishing the authentic oils from the adulterated samples of sesame oil and perilla oil, LDA was performed on the results of FA analysis to establish a predictive classification model. The prediction results for authentic and adulterated oil samples blended with cheaper oils, corn oil, and soybean oil, are summarised in Table 3. Among the five variables (palmitic, stearic, oleic, linoleic, and linolenic acids), stearic acid (Wilk's λ = 0.632) and palmitic acid (Wilk's λ = 0.407) showed the highest discriminant power for adulterated sesame oils and perilla oils, respectively. The first discriminant function was used for statistical analysis (Wilk's λ = 0.246, p = 0.000, and canonical correlation = 0.868 for the adulterated sesame oils; Wilk's λ = 0.300, p = 0.000, and canonical correlation = 0.837 for the adulterated perilla oils). The unstandardised canonical discriminant function coefficient (Z) assigns a sample to predicted group (authentic oil or adulterated oil). The value of Z was calculated by these equations: Z = -1003.505 + (8.899 × palmitic) + (13.719 × stearic) + (9.772 × oleic) + (10.246 × linoleic) + (13.525 × linolenic) for the sesame oils; Z = -9.385 + (1.494 × palmitic) + (-4.697 × stearic) + (0.342 × oleic) + (0.343 × linoleic) for the perilla oils. The variable of linolenic acid was not used for the LDA of perilla oils. Generally, If Z > 0, a sample is assigned to the authentic oil group for sesame oils, whereas if Z < 0, a sample is assigned to the adulterated oil group. In the case of perilla oils, the value of Z was the opposite. The Fisher's linear discriminant function was employed to classify the group for each oil. As shown in Table 3, the correctly classified rate was 100% for sesame oils and 96.8% for perilla oils. Only the adulterated perilla oil mixed with 2% soybean oil was misclassified into the authentic oil group.

Conclusion

The goal of the present work was to investigate the FA composition of 11 types of edible vegetable oils marketed in South Korea, and to characterise their FA distribution pattern. The unique FA profiles of vegetable oils showed the differences in the value of SFA, MUFA, and PUFA. Coconut oil (93.3%) showed the highest value of SFA, whereas canola oil (60.58%) and olive oil (76.44%) showed the highest value of MUFA due to the large presence of linoleic acid. The perilla oil (80.14%), flaxseed oil (73.45%), and grapeseed oil (70.44%) showed the highest content of PUFA which has been considered as a beneficial vegetable oil owing to the action of lowering cholesterol level. The content of α-linolenic acid of perilla oil (68.16%) was comparatively higher than that of the other vegetable oils, and the unique characteristics can make it possible to be used as functional oil in spite of the drawback of easily being oxidised. Rice bran oil (1.69) and olive oil (0.56) had the ideal ratio of TPUFA/TSFA recommended by WHO. The ideal ratio of omega-6/omega-3 FAs was observed in soybean oil (8.65) and olive oil (10.95). The FAs data of vegetable oils could be used for

Table 3. Summary of prediction results obtained by linear discriminant analysis for authentic and adulterated oil samples.

Actual group	Predicted group		
	Authentic oil	Adulterated oil	Correctly classified rate (%)
Authentic sesame oils (n = 27)	27	0	100
Adulterated sesame oils (n = 6)	0	6	100
Total correct classification (%)	(27+6)/33 = 100		
Authentic perilla oils (n = 25)	25	0	100
Adulterated perilla oils (n = 6)	1	5	83.3
Total correct classification (%)	(25+5)/31 = 96.8		

assessing the nutritional intake of Korean population, and will provide basic information for recommended daily consumption. Chemometric approaches utilise multivariate statistics to extract and collect useful information from numerous analytical data. In the present work, multivariate statistical techniques including PCA and CA were applied to the experimental data obtained from GC-FID for differentiating and visualising the groups of vegetable oils. The principal component scores plot and dendrogram showed that the eleven kinds of vegetable oils are grouped into three clusters. It was confirmed that the linolenic acid content and iodine value, the specification of quality inspection for sesame oils and perilla oils distributed in Korea, are not appropriate for detecting the adulterated oils which are blended with a small amount of cheaper oils. Meanwhile, the combined approach of using LDA and of analysing FA contents could be an alternative tool for distinguishing the economically motivated adulteration of sesame oil and perilla oil from authentic ones, and it will also act as a critical parameter in quality control.

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