

# Relationship Between Geographical Origin and Fatty Acid Composition of Turkish Virgin Olive Oils for Two Harvest Years

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**Abstract** In this study, the fatty acid compositions of Turkish virgin olive oils produced in the Izmir province, an important olive production region of Turkey, were classified by chemometric methods: principal component analysis (PCA) and discriminant analysis (DA). A total of 103 oil samples were examined over the course of two harvest years (2001–2002 and 2002–2003). The samples were divided into five groups according to olive growing zones: North (Ayvalik cultivar), East (Memeli, Memecik, Domat and Gemlik cultivars), South (Memecik cultivar), Izmir Peninsula (Erkence cultivar) and Firms (poly-varietal oils or commercial blends). Consistent with discriminant analysis (DA), the predicted grouping in terms of the two harvest years were correctly separated as 84.6 and 85.9%, respectively. The highest levels of predicted grouping for the two harvest years were found in the North (Ayvalik cultivar) and Izmir peninsula (Erkence cultivar) groups (as 100%). In addition to oleic, linoleic, linolenic, margaric and margoleic acids, total *trans* isomers of linoleic, linolenic and palmitic/linoleic were determined to be the best descriptive components for the oil samples.

**Keywords** Virgin olive oils · Turkey · Fatty acids · Principal component analysis · Discriminant analysis · Geographical origin

## Introduction

Virgin olive oil, obtained from the fruits of olive trees (*Olea europaea* L.), is of special interest to consumers due to its unique sensory properties and health benefits. The importance of virgin olive oil, the main oil source of the traditional Mediterranean diet, arises from its high level of monounsaturated fatty acids (mainly oleic acid) and the presence of natural antioxidants such as phenols, tocopherols and carotenoids. The health advantages are due largely to its fatty acid composition, particularly the oleic acid and MUFAs, and the naturally occurring antioxidants [1, 2].

One of today's major problems in the agro-food industry, including the olive oil sector, is to identify objective tools to trace raw materials, like virgin olive oil from certain locations or cultivars, as well as finished products from the producer to the consumer. The authenticity and traceability of virgin olive oil are of great importance for the protection of the consumer. Determination of the compositional variability of virgin olive oils produced from certain location or cultivar is necessary for the proper classification of oils as well as for prevention of blending monocultivar oils. The chemical composition of virgin olive oils might differ due to geographical, agronomic and technological influences. Differences in composition due to geographic origin provide the basis of legislation such as protected denomination of origin (PDO) and protected geographical indication (PGI). PDO and PGI certification enables labeling of food products by growing area, and

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provides extra economical benefits for producers of designated areas. The PDO of three zones (Edremit Gulf Olive Oils, Ayvalik Olive Oils and South Aegean Olive Oils) have been certified by the Turkish Patent Institute to authenticate oils produced from two economically important domestic cultivars (Ayvalik and Memecik) of the main olive growing regions of Turkey [3].

Major and/or minor components such as triacylglycerols, fatty acids and sterols in combination with chemometrics have been employed for the classification and characterization of virgin olive oils based on cultivar, geographical origin and harvest year. Among the components of olive oil, fatty acid profiles are extremely useful for characterization and discrimination of an olive cultivar or its geographical location [4]. There are several studies on geographical characterization of virgin olive oils from Turkish [5–8] and northern countries of the Mediterranean basin [9–14] based on fatty acid profiles.

In recent years, multivariate statistical methods, such as principal component analysis (PCA), hierarchical cluster analysis (HCA), discriminant analysis (DA) and classification analysis (CA), have been used extensively to classify and characterize virgin olive oils based on their geographical origins. The PCA method, one of the simplest and most used methods, is based on variable reduction by linear combination of initial variables that define principal components (PC). It is possible to reduce the set of variables without losing essential initial information [4, 15, 16]. The data produced by instrumental chromatographic techniques, gas chromatography (GC) and high pressure liquid chromatography (HPLC), for the characterization of virgin olive oil from different locations or cultivars are evaluated with these sophisticated methods (PCA, HCA, CA and DA). Multivariate statistical (PCA, DA or CA) evaluation of data is not a solution, but is a very promising approach for the evaluation of analytical data as to the geographical origin of a virgin olive oil sample. However, some studies have attempted to verify and classify the origins of certain virgin olive oils from major olive oil-producing countries (Italy, Spain, France, Greece—and nowadays Turkey), using their fatty acid profiles aided by multivariate statistical methods, such as PCA, HCA and DA [4, 5, 8, 10, 12, 13, 16–21]. Although Turkey is the world's fifth largest producer of olive oil (5%) and contributes 11.3% to the world's exports [22], there is a lack of data elucidating the characterization and classification of olive oil produced and marketed in Turkey.

This study addresses the need to evaluate by chemometric methods, PCA and DA, the classification and discrimination of virgin olive oils originating from Turkey based on the fatty acid profile, a reliable indicator for the discrimination and classification of oils of PDO.

## Materials and Methods

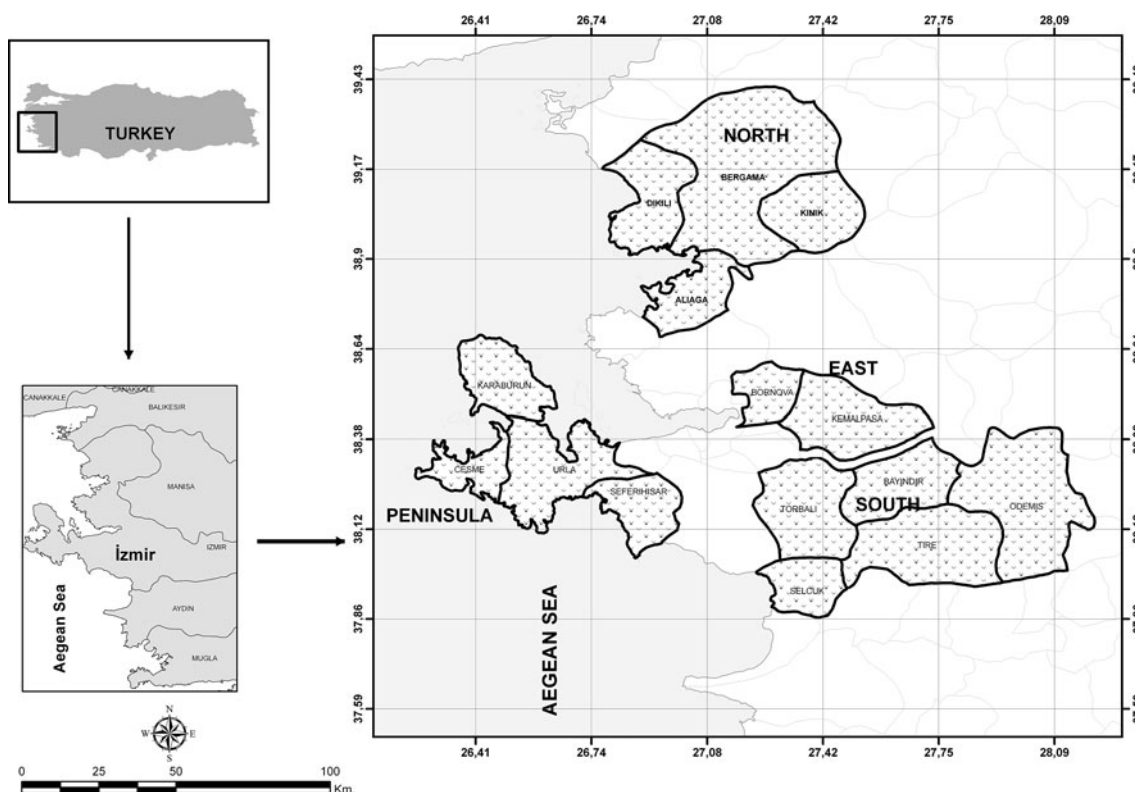
### Material

The virgin olive oil samples were collected from plants utilizing a number of different processing systems: classical systems (hydraulic presses—known as the wet system, and super presses—the dry system) and continuous systems (three phase, dual phase and sinolea) in the Izmir province between November and February of two consecutive harvest years (2001–2002 denoted by 1 and 2002–2003 denoted by 2). These samples were divided into five sub-groups based on the important olive cultivation districts of the Izmir province:

1. The North (N) sub-group: This sub-group contains Ayvalik olive varieties widely grown in locations in the north zones: Aliaga, Bergama, Yeni Sakran, Kinik, Candarli and Dikili. This cultivar is locally known as Edremit, Edremit Yağlık, Şakran, Midilli and Ada Zeytini [23, 24].
2. The East (E) sub-group: Locations of this sub-group were Kemalpaşa and Orchard of Olive Research Institute. The different olive cultivars include Memeli, Memecik, Domat and Gemlik [23, 24].
3. The South (S) sub-group: Memecik olive cultivar, known under locally names as Tas arasi, Asiyeli, Gulumbe, Sehir and Yagliik, is grown in the south zones (Odemis, Tire, Torbali, Bayindir and Selcuk) [23, 24].
4. Izmir Peninsula (IP) sub-group: Erkence, known locally as Hurma Kaba and Hurma Erkence, is the primary domestic olive cultivar of this section. Locations of this sub-group were Urla, Seferihisar, Mordogan and Karaburun [23, 24].
5. Firms (F) samples sub-group: This group covers the blended commercial virgin olive oil samples of unknown locations or domestic olive cultivar(s). These poly-varietal oils were packaged and labelled by various firms in Izmir.

A map of the live growing zones in the Izmir province is given in Fig. 1. A total of 103 virgin olive oil samples were collected from five sub-groups in the Izmir province during two harvest years. Thirty-nine (39) of these samples were from the 2001–2002 harvest year and 64 oil samples were collected from the 2002–2003 harvest year.

The fatty acid profiles were determined using a capillary gas chromatographic method described by the European Union Commission [25]. Fatty acid methyl esters (FAMES) were prepared by treatment with sodium methylate according to a cold methylation method [26]. A gas chromatograph (HP 6890) using a capillary column DB-23 (30 m × 0.25 mm ID and 0.25 µm film thickness 50%



**Fig. 1** Geographical areas of the four olive growing zones in İzmir Province

cyanopropyl, J & W Scientific, Folsom, CA, USA) was employed. The oven temperature was programmed from 170 to 210 °C at 2 °C/min and then held at 210 °C for 10 min. The carrier gas was helium (0.5 ml/min) and the injector and detector (FID) temperatures were 250 °C. The split ratio was 1:100 and the injected volume was 0.2 µl. Each sample was injected in triplicate ( $n = 3$ ). Fatty acid standards had linear calibration curves through the origin ( $R^2 = 0.99$ ). The GC method was validated for fatty acid determination of oil samples within 95% confidence limits. A standard FAME mixture was used as a standard (Sigma-Aldrich Chemicals 189-19). All fatty acid peak areas were calculated by HP 3365 Chemstation program and recorded as peak area percentages [27].

PCA, a common technique for finding patterns in data of high dimensions, and Linear Discriminant Analysis (LDA) with cross-validation (CV), were performed. The statistical package SPSS version 15.0 was used (SPSS 2001) for multivariate analysis [28].

## Results and Discussion

The virgin olive oil samples were characterized according to their fatty acid profiles and five individual parameters: palmitic (p) C16:0; palmitoleic (po) C 16:1n-7; margaric (m) C

17:0; margaroleic (mo) C 17:1n-8; stearic (s) C 18:0; oleic (o) C 18:1n-9; Linoleic (l) C18:2n-6; Linolenic (ln) C18:3n-3; Arachidic (a) C 20:0; gadoleic (g) C 20:1n-9; behenic (b) C 22:0; lignoseric (lg) C 24:0; elaidic (ea) C 18:1*t*; *trans* linoleic (C 18:2 *t*) + *trans* linolenic (C 18:3*t*) (tlln) and Total Trans FA (tfa); Oleic/Linoleic (ol); Palmitic/Linoleic (pl); Linoleic/Linolenic (lln); Squalene (Sq). The statistical parameters of fatty acid profiles for two harvest years (2001–2002 and 2002–2003) are reported in Table 1.

The fatty acid composition is a quality parameter and an authenticity indicator of virgin olive oils. As shown in Table 1, numerous *cis-trans* isomers of fatty acids were detected in the oil samples produced from important domestic olive varieties grown in İzmir province. A typical chromatogram of a virgin oil sample extracted by classical hydraulic press in South part (Selçuk) of İzmir province for 2002/2003 harvest years is shown in Fig. 2.

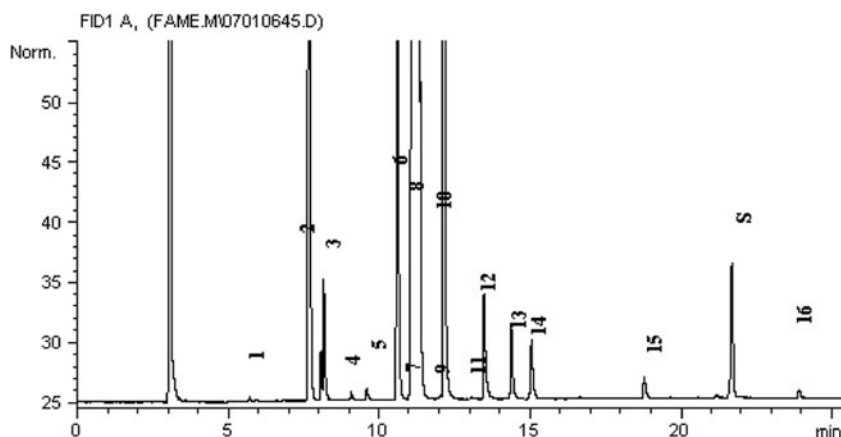
As can be seen in Table 1, the range for individual fatty acids during two harvest years virtually covered the full range of the IOOC [29] and the Turkish Food Codex standards [30]. The linolenic acid (18:3n-3) level of virgin olive oil samples in the İzmir province was below the maximum value fixed by the IOOC (1.0%) [29] and by the Turkish Codex (0.9%) [30]. The contents of linolenic acid were between different ranges for the two harvest years (Table 1). The linolenic acid range (0.43–1.00%) from the

**Table 1** Statistical parameters for the fatty acid composition of Turkish virgin olive samples collected during two harvest years (2001–2002 and 2002–2003)

| Functions | Harvest year 2001–2002 ( <i>N</i> = 39) |       |                             | Harvest year 2002–2003 ( <i>N</i> = 64) |       |                             |
|-----------|---|-------|-----------------------------|---|-------|-----------------------------|
|           | Min                                     | Max   | Mean and standard deviation | Min                                     | Max   | Mean and standard deviation |
| p         | 9.62                                    | 18.97 | 13.18 ± 1.61                | 10.81                                   | 14.44 | 12.13 ± 0.84                |
| po        | 0.63                                    | 1.22  | 0.85 ± 0.14                 | 0.62                                    | 1.13  | 0.78 ± 0.09                 |
| m         | 0.04                                    | 0.20  | 0.13 ± 0.04                 | 0.03                                    | 0.14  | 0.10 ± 0.04                 |
| mo        | 0.06                                    | 0.28  | 0.20 ± 0.06                 | 0.06                                    | 0.24  | 0.16 ± 0.06                 |
| s         | 2.43                                    | 3.54  | 2.85 ± 0.28                 | 1.42                                    | 3.38  | 2.46 ± 0.25                 |
| o         | 62.90                                   | 76.92 | 69.17 ± 3.16                | 68.26                                   | 77.16 | 73.13 ± 2.50                |
| l         | 8.08                                    | 17.17 | 11.87 ± 2.32                | 6.26                                    | 14.53 | 9.75 ± 1.95                 |
| ln        | 0.43                                    | 1.00  | 0.68 ± 0.13                 | 0.37                                    | 0.81  | 0.56 ± 0.08                 |
| a         | 0.22                                    | 0.53  | 0.41 ± 0.05                 | 0.33                                    | 0.54  | 0.40 ± 0.04                 |
| g         | 0.22                                    | 0.50  | 0.31 ± 0.05                 | 0.24                                    | 0.38  | 0.310 ± 0.03                |
| b         | 0.07                                    | 0.19  | 0.11 ± 0.02                 | 0.09                                    | 0.16  | 0.12 ± 0.02                 |
| lg        | 0.00                                    | 0.08  | 0.05 ± 0.01                 | 0.03                                    | 0.08  | 0.05 ± 0.01                 |
| ea        | 0.00                                    | 0.08  | 0.01 ± 0.01                 | 0.004                                   | 0.03  | 0.01 ± 0.005                |
| tln       | 0.03                                    | 0.11  | 0.07 ± 0.02                 | 0.01                                    | 0.10  | 0.05 ± 0.02                 |
| tfa       | 0.04                                    | 0.16  | 0.09 ± 0.03                 | 0.02                                    | 0.12  | 0.06 ± 0.02                 |
| ol        | 3.85                                    | 9.52  | 6.09 ± 1.54                 | 4.74                                    | 12.29 | 7.88 ± 1.96                 |
| pl        | 0.63                                    | 1.76  | 1.15 ± 0.26                 | 0.80                                    | 1.82  | 1.29 ± 0.25                 |
| lln       | 10.82                                   | 39.93 | 18.02 ± 4.65                | 10.16                                   | 26.76 | 17.77 ± 4.68                |
| Sq        | 0.21                                    | 1.24  | 0.46 ± 0.21                 | 0.25                                    | 0.99  | 0.56 ± 0.16                 |

p Palmitic, po palmitoleic, m margaric, mo margaroleic, s stearic, o oleic, l linoleic, ln linolenic, a arachidic, g gadoleic, b behenic, lg lignoseric, ea elaidic, tln *trans* linoleic + linoleic, tfa total *trans* fa, ol oleic/linoleic, pl palmitic/linoleic, lln linoleic/linolenic, Sq squalene

**Fig. 2** A typical chromatogram of a virgin oil sample extracted by classical hydraulic press in the southern part (Selcuk) of the Izmir province for the 2002/2003 harvest year 1 myristic, 2 palmitic (*p*), 3 palmitoleic (*po*), 4 margaric (*m*), 5 margaroleic (*mo*), 6 stearic (*s*), 7 elaidic (*ea*), 8 oleic (*o*), 9 *trans* linoleic (Linoelaidic acid), 10 linoleic (*l*), 11 *trans* Linolenic, 12 linolenic (*ln*), 13 arachidic (*a*), 14 gadoleic (*g*), 15 behenic (*b*), 16 lignoseric (*lg*)



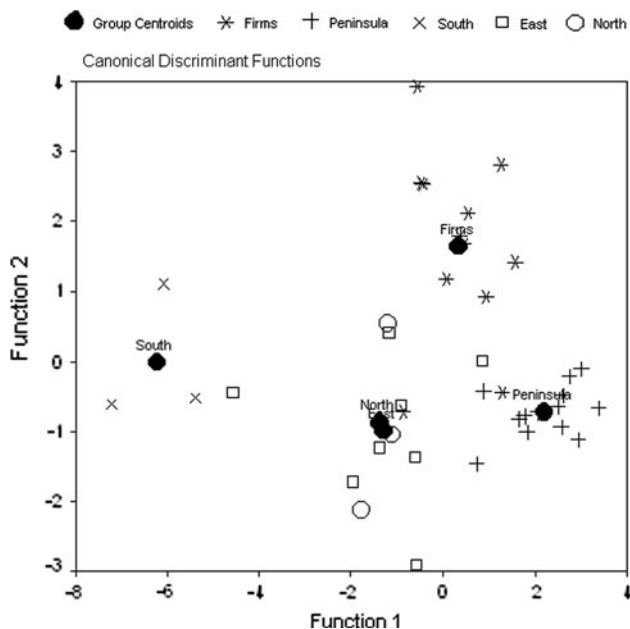
first harvest year (2001–2002) was broader than the range (0.37–0.81%) of the second harvest year (2002–2003). The differences were remarkable for oleic acid, the major fatty acid of olive oil. The range of oleic acid values (18:1n-9) was determined for two harvest years (Table 1). The oleic acid levels (68.26–77.16%) for the second harvest year (2002–2003) were generally higher than those (62.90–76.92%) of the first harvest year (2001–2002). The linoleic acid (18:2n-6) levels for the two harvest years ranged from 10.9–13.9% and 8.7–11.80%, respectively (Table 1). The

nutritional (18:2/18:3, l/ln) fatty acid ratios (a value considered to be optimal) of the oil samples of domestic cultivars ranged from 10.82–39.93 to 10.16–26.76 for the two harvest years, respectively. It is reported that the ratio of linoleic/linolenic correlates with the bitterness and green perception of oils due to the contribution of volatile compounds to virgin olive oil flavor. For example, (E)-hex-2-enal contributes to the green odor but also imparts an intense bitter taste. Empirical results on the subject state that the lower the ratio, the higher the bitterness [31].

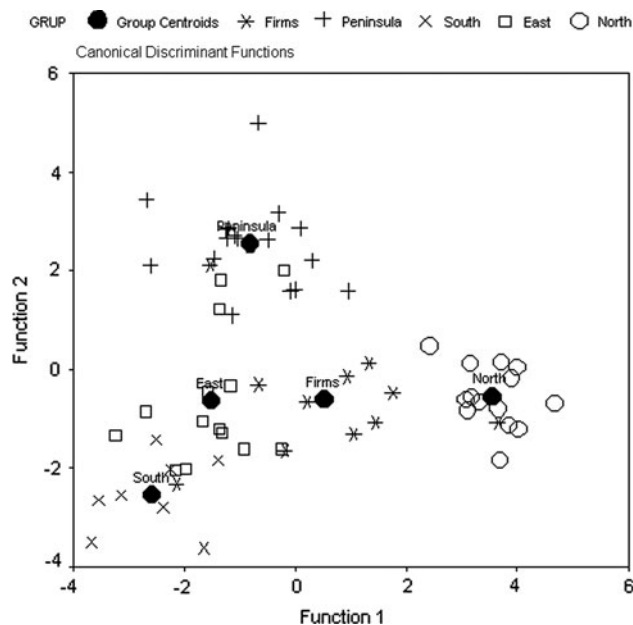
**Table 2** Variance values explained by the principal components for Turkish virgin olive oil samples collected during two crop years (2001–2002 and 2002–2003)

| Principal components | Crop year 2001–2002 ( <i>n</i> = 39) |            |                  | Crop year 2002–2003 ( <i>N</i> = 64) |            |                  |
|----------------------|--------------------------------------|------------|------------------|--------------------------------------|------------|------------------|
|                      | Eigenvalue                           | Variance % | Total variance % | Eigenvalue                           | Variance % | Total variance % |
| p                    | 28.597                               | 64.567     | 64.567           | 33.716                               | 92.043     | 92.043           |
| po                   | 12.871                               | 29.060     | 93.627           | 1.712                                | 4.673      | 96.716           |
| m                    | 2.573                                | 5.809      | 99.435           | 0.966                                | 2.637      | 99.353           |
| mo                   | 0.131                                | 0.296      | 99.732           | 0.114                                | 0.310      | 99.663           |
| s                    | 0.051                                | 0.114      | 99.846           | 0.066                                | 0.181      | 99.844           |
| o                    | 0.028                                | 0.064      | 99.910           | 0.039                                | 0.106      | 99.950           |
| l                    | 0.028                                | 0.063      | 99.973           | 0.011                                | 0.031      | 99.981           |
| ln                   | 0.005                                | 0.010      | 99.983           | 0.003                                | 0.007      | 99.988           |
| a                    | 0.003                                | 0.008      | 99.991           | 0.002                                | 0.006      | 99.994           |
| g                    | 0.002                                | 0.004      | 99.995           | 0.001                                | 0.003      | 99.997           |
| b                    | 0.001                                | 0.002      | 99.997           | 0.000                                | 0.001      | 99.998           |
| lg                   | 0.001                                | 0.001      | 99.998           | 0.000                                | 0.001      | 99.999           |
| ea                   | 0.000                                | 0.001      | 99.999           | 0.000                                | 0.001      | 99.999           |
| tln                  | 0.000                                | 0.000      | 100.000          | 0.000                                | 0.000      | 100.000          |
| tfa                  | 6.62E-005                            | 0.000      | 100.000          | 5.141E-5                             | 0.000      | 100.000          |
| ol                   | 3.38E-005                            | 7.64E-005  | 100.000          | 2.382E-5                             | 6.503E-5   | 100.000          |
| pl                   | 2.46E-005                            | 5.56E-005  | 100.000          | 1.189E-5                             | 3.245E-5   | 100.000          |
| lln                  | 2.10E-005                            | 4.75E-005  | 100.000          | 8.558E-6                             | 2.336E-5   | 100.000          |
| Sq                   | 8.75E-008                            | 1.98E-007  | 100.000          | 8.671E-7                             | 2.367E-6   | 100.000          |

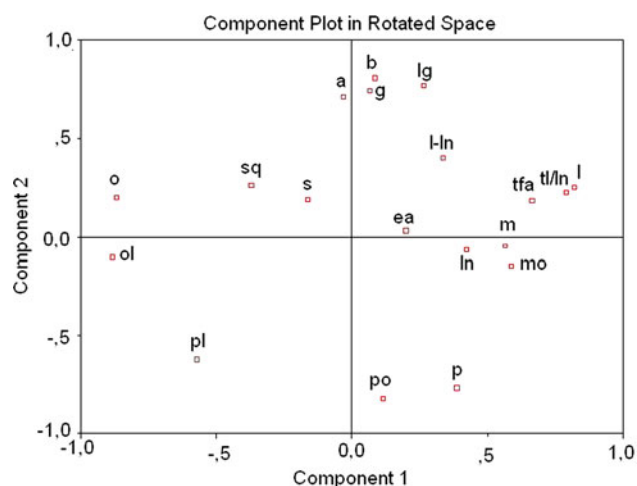
*p* Palmitic, *po* palmitoleic, *m* margaric, *mo* margaroleic, *s* stearic, *o* oleic, *l* linoleic, *ln* linolenic, *a* arachidic, *g* gadoleic, *b* behenic, *lg* lignoseric, *ea* elaidic, *tln* *trans* linoleic + linoleic, *tfa* total *trans* fa, *ol* oleic/linoleic, *pl* palmitic/linoleic, *lln* linoleic/linolenic, *Sq* squalene



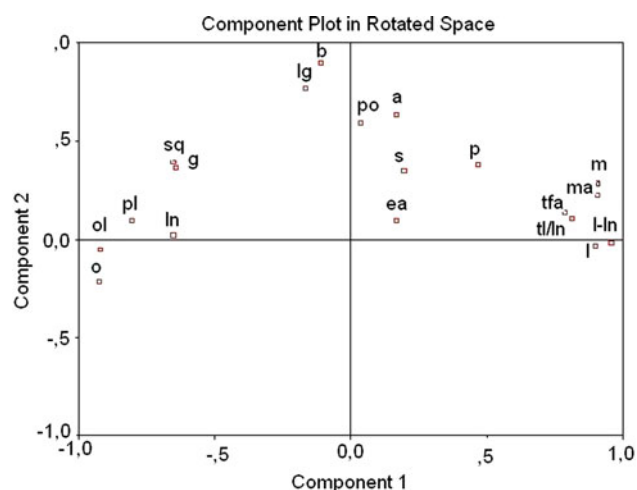
**Fig. 3** Score plot of samples on the plane identified by the first two function for 39 virgin olive oil samples in harvest year 2001–2002



**Fig. 4** Score plot of samples on the plane identified by the first two function for 64 virgin olive oil samples in harvest year 2002–2003



**Fig. 5** Plot of the weights of the original set of variables on the plane of the first two components (fatty acid profiles) for 39 virgin olive oil samples in harvest year 2001–2002



**Fig. 6** Plot of the weights of the original set of variables on the plane of the first two components (fatty acid profiles) for 64 virgin olive oil samples in harvest year 2002–2003

The distribution of fatty acids in virgin oil samples was in agreement with those of commercial and monocultivar oils collected from different locations in Turkey [5–8] and countries of the Mediterranean basin [9–14, 17–21]. The variations in fatty acid profile of oil samples differ slightly, depending on the olive cultivar, growing conditions, harvest time and locations. Primary factors affecting fatty acid contents, especially oleic acid level, may originate from latitude, climate, olive cultivar and/or stage of fruit maturity during harvest [6, 8, 9, 12, 13, 18, 31].

Virgin olive oils are classified into two types based on their fatty acid compositions. The first type of olive oil is characterized by low linoleic and palmitic and high oleic levels. The second type is characterized by high linoleic and palmitic and low oleic levels. The virgin olive oils of

the North Mediterranean (Spanish, Italian, Turkish and Greek) are of the first type, while North African origin oils, especially Tunisian, are of the second type [1, 2].

With respect to the analysis, levels of total *trans* isomers for the oils samples ranged among 0.04–0.16% and 0.02–0.12% for the two harvest years, respectively. According to official norms, total *trans* fatty acids in virgin olive oils should be 0.1% maximum. The total levels of *trans* fatty acid isomers [sum of elaidic acid (C 18:1 *t*) and (C 18:2 *t* + C 18:3 *t*)] of most of the oil samples were generally within acceptable IOOC regulation limits [29], and the Turkish Food Codex standards [30]. The distribution of *trans* fatty acids was similar to those reported in Turkish virgin olive oils by Diraman and Dibeklioglu [8].

Olive oil contains large amounts of squalene, a terpenoid hydrocarbon, with antioxidant properties. Squalene levels for the two harvest years ranged from 0.21–1.24% to 0.25–0.99 1.22%, respectively. The differences in squalene levels between olive oils may depend on the specific cultivar and the altitude at which the trees are grown [2]. These findings are generally in accordance with French [21] and Turkish [8] olive oils.

To select the best model with the minimum number of dimensions explaining the data structure, PCA was applied (using fourteen fatty acids components) to the grouped oil samples (total of 106) according to their locations. The exclusion rule employed was based on the amount of residual variability to tolerate [32], retaining a sufficient number of PC's capable of explaining a percentage of variance >80% or when the contribution of the ( $p + 1$ ) th component to variance explained was very small (<5%). Using this rule, the first two PC is sufficient because they described 93.63 and 96.72% of the sample variability (Table 2). This is in accordance with criteria of Jolliffe [33, 34] which suggests rejecting those PC having eigenvalues <0.7.

The first two functions and the relative weight of the original data set from the two harvest years are given in Figs. 3 and 4, respectively. Also, shown in Figs. 5 and 6, are the plots of the weights of the original set of variables on the plane of the first two PCs from the two harvest years, respectively.

Analysis of PCA results showed that the first principal component (PC1) and the second principal component (PC2) explained 64.57 and 29.06% of the total variance (Table 2), respectively for the first harvest year (2001–2002). Also, these values are highly correlated to margaric (m), oleic (o), linolenic (ln), elaidic (ea), *trans* linoleic + *trans* linolenic (tlln), palmitic/linoleic (pl) and linoleic/linolenic (lln) for PC1, and margaroleic (mo), linoleic (l), behenic (b), lignoceric (lg) and total *trans* fatty acids (tfa) for PC 2, respectively (Fig. 5). These fatty acids best describe the virgin olive oil samples in 2001–2002 harvest year.

**Table 3** Canonical discriminant analysis for virgin olive oil samples collected from Izmir province for two harvest years (2001–2002 and 2002–2003)

| Harvest year 2001–2002 ( <i>N</i> = 39) |                    |            |                       |                   | Harvest year 2002–2003 ( <i>N</i> = 64) |            |                       |                   |
|---|--------------------|------------|-----------------------|-------------------|---|------------|-----------------------|-------------------|
| Canonical discriminant function         | Eigenvalue         | Variance % | Canonical correlation |                   | Eigenvalue                              | Variance % | Canonical correlation |                   |
| 1                                       | 12.85 <sup>a</sup> | 45.5       | 0.96                  |                   | 3.308 <sup>a</sup>                      | 59.7       | 0.876                 |                   |
| 2                                       | 9.92 <sup>a</sup>  | 35.2       | 0.95                  |                   | 1.963 <sup>a</sup>                      | 35.4       | 0.814                 |                   |
| 3                                       | 3.70 <sup>a</sup>  | 13.1       | 0.89                  |                   | 0.222 <sup>a</sup>                      | 4.0        | 0.426                 |                   |
| 4                                       | 1.75 <sup>a</sup>  | 6.2        | 0.80                  |                   | 0.045 <sup>a</sup>                      | 0.8        | 0.208                 |                   |
| Test of functions                       | Wilks' Lambda      | $\chi^2$   | DF                    | Significant level | Wilks' Lambda                           | $\chi^2$   | DF                    | Significant level |
| 1 through 4                             | 0.001              | 185.62     | 72                    | 0.000             | 0.061                                   | 163.32     | 16                    | 0.000             |
| 2 through 4                             | 0.007              | 121.23     | 51                    | 0.000             | 0.264                                   | 77.87      | 9                     | 0.000             |
| 3 through 4                             | 0.077              | 62.67      | 32                    | 0.001             | 0.783                                   | 14.32      | 4                     | 0.006             |
| 4                                       | 0.364              | 24.75      | 15                    | 0.053             | 0.957                                   | 2.58       | 1                     | 0.108             |

<sup>a</sup> First four canonical discriminant functions were used in the analysis

**Table 4** Mahalanobis distances between the oil origin groups for two harvest years (2001–2002 and 2002–2003)

| From                   | To      |         |         |           |         |
|------------------------|---------|---------|---------|-----------|---------|
|                        | East    | North   | South   | Peninsula | Firms   |
| 2001–2002 harvest year |         |         |         |           |         |
| East                   | 0       | 142.806 | 165.723 | 30.846    | 31.407  |
| North                  | 142.806 | 0       | 245.892 | 158.370   | 88.054  |
| South                  | 165.723 | 245.892 | 0       | 266.759   | 198.901 |
| Peninsula              | 30.846  | 158.370 | 266.759 | 0         | 36.915  |
| Firms                  | 31.407  | 88.054  | 198.901 | 36.915    | 0       |
| 2002–2003 harvest year |         |         |         |           |         |
| East                   | 0       | 28.552  | 9.462   | 13.692    | 12.123  |
| North                  | 28.552  | 0       | 45.030  | 29.164    | 14.717  |
| South                  | 9.462   | 45.030  | 0       | 30.246    | 16.665  |
| Peninsula              | 13.692  | 29.164  | 30.246  | 0         | 14.384  |
| Firms                  | 12.123  | 14.717  | 16.665  | 14.384    | 0       |

In the second harvest year (2002–2003), the first PC accounted for 92.04% of the total variance (Table 2) and was highly correlated to margaric (m), oleic (o), behenic (b) and palmitic/linoleic (pl). The second PC accounted for 4.67% of variance and is highly correlated to margoleic (mo), linoleic (l), lignoceric (lg) and *trans* linoleic + *trans* linolenic (tln) (Fig. 6). These parameters best described the oil samples from the second harvest year. Figures 3 and 4 showed that the all oil groups for the two harvest years are obviously separated due to the different domestic olive cultivars of the Izmir province.

In light of the chemometric analysis, oleic (o), linoleic (l), linolenic (ln), the major fatty acids in olive oil, and margaric (m), margoleic (mo), the minor fatty acids, as

well as total *trans* isomers of linoleic and linolenic (tln), and the palmitic/linoleic (pl) ratio were common parameters for the characterization of virgin olive oil from different locations for two harvest years. On the other hand, these parameters best describe the oil samples in the harvest year (2002–2003).

After PCA treatment, canonical discriminant analysis (Table 3) was applied to these parameters in order to classify the oil samples taken from the Izmir province into separate groups. The eigenvalue of the first crop year (2001–2002) associated with the first function contributed 45.5% to the variance of the original data and the second contributed 35.2%. The eigenvalue of the second crop year (2002–2003) associated with the first function contributed 59.7% to the variance of the original data and the second contributed 35.4%.

The Mahalanobis distances between the oil groups are shown in Table 4. The two closest origins (Mahalanobis  $D^2 = 30.85$ ) were East (different olive cultivars, like Memeli, Memecik, Domat and Gemlik) and Peninsula (Erkence olive cultivar) for first harvest year. Also, during, first year the South oil group (Memecik cultivar) was the most removed from the others with East being its closest neighbor (Mahalanobis  $D^2 = 165.72$ ). The two closest origins (Mahalanobis  $D^2 = 9.462$ ) were East and South for the second harvest year. The North oil (Ayvalik cultivar) was the most removed from the others with Firms (unknown origin) being its closest neighbor (Mahalanobis  $D^2 = 14.717$ ). Because there are five groups, only four discriminant functions can be calculated for the two harvest years.

The levels of predictive probability in the differentiation of groups concerning virgin olive oil samples for two crop years are shown in Table 5. Overall, 84.6% of the cross-

**Table 5** Classification results of Turkish virgin olive oils samples collected during two harvest years (2001–2002 and 2002–2003)

| Actual group | Harvest year 2001–2002 ( <i>N</i> = 39), predicting grouping <sup>a</sup> |       |      |       |           |       | Harvest year 2002–2003 ( <i>N</i> = 64), predicting grouping <sup>b</sup> |       |      |       |           |       |
|--------------|---|-------|------|-------|-----------|-------|---|-------|------|-------|-----------|-------|
|              | Number of cases   | North | East | South | Peninsula | Firms | Number of cases   | North | East | South | Peninsula | Firms |
| North        | 3   | 3     | 0    | 0     | 0         | 0     | 14  | 14    | 0    | 0     | 0         | 0     |
|              |   | 100.0 | 0.0  | 0.0   | 0.0       | 0.0   |   | 100.0 | 0.0  | 0.0   | 0.0       | 0.0   |
| East         | 8   | 2     | 4    | 1     | 1         | 0     | 14  | 0     | 10   | 1     | 3         | 0     |
|              |   | 25.0  | 50.0 | 12.5  | 12.5      | 0.0   |   | 0.0   | 71.4 | 7.1   | 21.4      | 0.0   |
| South        | 3   | 0     | 0    | 3     | 0         | 0     | 8   | 0     | 2    | 6     | 0         | 0     |
|              |   | 0.0   | 0.00 | 100.0 | 0.00      | 0.00  |   | 0.0   | 25.0 | 75.0  | 0.0       | 0.0   |
| Peninsula    | 13  | 0     | 0    | 0     | 13        | 0     | 17  | 0     | 0    | 0     | 17        | 0     |
|              |   | 0.0   | 0.0  | 0.0   | 100.0     | 0.0   |   | 0.0   | 0.0  | 0.0   | 100.0     | 0.0   |
| Firms        | 12  | 0     | 1    | 0     | 1         | 10    | 11  | 1     | 0    | 1     | 1         | 8     |
|              |   | 0.0   | 8.3  | 0.0   | 8.3       | 83.3  |   | 9.1   | 0.0  | 9.1   | 9.1       | 72.7  |

<sup>a</sup> Percentage of cross-validated cases correctly classified 84.6%

<sup>b</sup> Percentage of cross-validated cases correctly classified 85.9%

validated samples (total of 39) for first crop year (2001–2002) were correctly classified, while 100% from the North, 50% from the East, 100% from the South, 100% from Izmir Peninsula and 83.50% from the Firms were wrongly classified. Two East samples from the first harvest year were identified as North zone and one sample apiece were classified as South and Izmir peninsula. Two Firms oil samples from the first harvest year were identified as East and Izmir peninsula.

The data set (64 samples) for the second harvest year (2002–2003) showed that 85.9% of the cross-validated samples were correctly classified, while 100% from the North zone and Izmir Peninsula, 71.4% from the East, 75% from the South and 72.7% from the Firms were wrongly classified. All North zone and Izmir peninsula samples for both harvest years were correctly classified. Three East samples from the second harvest year were classified as Izmir peninsula and one was identified as South. Two South samples for the second harvest year were identified as East group. Three Firms oil (unknown origin) samples from the second harvest year were classified as North, South and Izmir peninsula, respectively. Cumulatively 16.60 and 27.30% of the Firms oils for both harvest years, respectively, were recognized as belonging to known groups (cultivar oils) on the basis of fatty acid profile. These relationships among oil groups during two harvest years appeared to be due to the homogenous or heterogeneous olive cultivar areas, commercial blending depend on olive and oil exchanges among olive growing zones in the Izmir province and blend oil production from different sources inside or outside of the Izmir province.

Similar investigations based only on fatty acid compositional data for Greek [16, 18], Italian [12, 17, 19], Spanish [10, 13, 20], French [22] and Turkish [5, 8] oils

resulted in a few defined regions and crop years. These studies were carried out using different software packing programs (SAS, SPSS, SIMCA), including PCA, HCA and DA.

The results of this study showed that application of chemometric methods, PCA and DA, to fatty acid composition is quite successful for the classification of virgin olive oil samples with respect to variety, geographical origin and harvest year, as a model based on the Izmir province. On the other hand, it was indicated that the discrimination results from the North and Izmir cultivar zones would correctly be classified for monovarietal or growing area using fatty acid profiles. The Ayvalik, Memecik and Erkence oils from different growing regions could be differentiated based on their fatty acid profiles with PCA and DA results. This research is a step towards the subjective characterization and classification of economically important areas in oil production for utilization in the Turkish food industry. Use of the multivariate approach on the fatty acid profiles of virgin olive oil taken from three sections of the Izmir province during two crop years appears to be advantageous for reducing the data set compressing the variance into a smaller number of axes. The results of this investigation give us the possibility of evaluating data to control labelling and of building up the reference set necessary for establishing the criterion of geographical origin, especially the Izmir province, and ultimately increasing the competitiveness of these products on the market.

Future work on the characterization of virgin olive oils of the Izmir province should be carried out with investigations covering different parameters (triacylglycerols, sterols, phenolic compounds and volatile compounds) in terms of building a more comprehensive data bank.



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