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Food Chemistry 97 (2006) 382–393
Food Chemistry
www.elsevier.com/locate/foodchem

Differentiation of French virgin olive oil RDOs by sensory characteristics, fatty acid and triacylglycerol compositions and chemometrics

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Received 10 January 2005; received in revised form 28 April 2005; accepted 28 April 2005

Abstract

The sensory and chemical characteristics (fatty acid and triacylglycerol compositions) of the five registered designations of origin (RDOs) of French virgin olive oils ('Aix-en-Provence', 'Haute-Provence', 'Nyons', 'Nice' and 'Vallée des Baux de Provence') ($n = 539$) were determined over a six year harvest period. The evaluation of fruity, bitter and pungent oils was insufficient for describing the RDOs, so it was necessary to complete the olive description with descriptive attributes (analogical describers) put forth by the tasters. All the isomers were taken into account to determine the fatty acid composition. The utilisation of propionitrile, instead of the mixture of acetone/acetonitrile, leads to a better separation of the triacylglycerols especially of the crucial pairs LOO + PLnP/PoOO, PLO + SLL/PoOP, SOL/POO. The fatty acid and triacylglycerol compositions make up a data bank of the five French RDOs. A linear discriminant analysis applied to the samples, described by 37 parameters, allow us to perfectly differentiate the RDOs: 'Nyons', 'Nice' and 'Haute-Provence'. The 'Aix-en-Provence' and 'Vallée des Baux de Provence' RDOs, which are separate from the three other RDOs, are not completely differentiated. In fact, these two poly-varietal RDOs have two principal varieties in common: Salonenque and Aglandau which, at different levels, explains the established resemblances.

Keywords: Virgin olive oils; RDO; PDO; Sensory characteristics; Fatty acids; Triacylglycerols; Chemometrics

1. Introduction

One of today's major problems in the agricultural-food industry is to set down objective tools in order to determine the traceability of raw materials as well as finished products so that we can follow the products from the producer to the consumer.

France is a modest producer of virgin olive oils with about 4000 tons annually, while consumption in 2003 was about 97,000 tons. This deficit on one hand and the rising interest of consumers for the Mediterranean diet, as well as an information and advertising campaign on the other hand, have brought about a revival in the French olive oil industry. The French olive

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doi:10.1016/j.foodchem.2005.04.024

growers have chosen quality and the pursuit of authenticity for a type of oil that is found today in the five registered designations of origin (RDO) (AOC in French) which represent about 30% of the national production. Four of these oils have obtained recognition on the European level: protected designation of origin (PDO) (AOP in French).

Virgin olive oil is one of the rare agricultural food products that undergoes a standard sensory evaluation on top of chemical analysis (EEC Regulation, 1991). These analyses which are based on the perception of defects, allow the classification of olive oils into three categories: extra virgin, virgin or lampante virgin. The RDOs are regulated by agricultural and practice specifications. No chemical parameter is set for these RDOs except for acidity. A sensory description has been done by professional trade associations which are responsible for the different RDOs. This information is largely insufficient for characterising these oils.

Traceability and the authenticity of olive oils have been the object of numerous studies in the past few years using extremely varied physical–chemical determinations in association with chemometric analyses: fatty acids (Alonso Garcia & Aparicio Lopez, 1993; Bucci, Magri, Magri, Marini, & Marini, 2002; Forina & Tiscornia, 1982; Stefanoudaki, Kotsifaki, & Koutsaftakis, 1999; Tsimidou & Karakostas, 1993); fatty acids and triacylglycerols (Aranda, Gómez-Alonso, Rivera del Álamo, Salvador, & Fregapane, 2004; Tsimidou, Macrae, & Wilson, 1987); sterols (Leardi & Paganuzzi, 1987); ^{1}H and ^{13}C NMR (Mannina, Patumi, Proietti, Bassi, & Segre, 2001; Vlahov, Shaw, & Kell, 1999; Vlahov, Del Re, & Simone, 2003); isotopic ratios $^{13}C/^{12}C$, $^{18}O/^{16}O$ (Angerosa et al., 1999; Bianchi, Angerosa, Camera, Reiniero, & Anglani, 1993); near-infrared spectroscopy (NIR) (Bertran et al., 2000); Fourier transform infrared spectroscopy (FTIR) (Tapp, Defernez, & Kemsley, 2003); electronic nose (Guadarrama, Rodriguez-Méndez, Sanz, Rioz, & de Saja, 2001); aromas (Angerosa, 2002; Morales, Aparicio, & Rios, 1994; Servili, Selvaggini, Taticchi, & Montedoro, 2000; Zunin et al., 2004). We recently demonstrated (Ollivier, Artaud, Pinatel, Durbec, & Guérère, 2003) that the determination of fatty acid and triacylglycerol compositions, taking into account the different isomers, associated with statistical methods of data processing, allowed us to characterise the oils of the principal French cultivars as well as two RDOs.

This study is part of a wider work (Moutier et al., 2004) for the characterisation of French virgin olive oils. Its aim is to determine the principal sensory characteristics and the fatty acid and triacylglycerol compositions of the virgin olive oils of the five French RDOs in order to create a data bank which will permit us to determine the origin of these oils.

2. Materials and methods

2.1. Materials

Industrial virgin olive oil samples ($n = 539$) were obtained from the French Inter-Professional Olive Oil Association (AFIDOL), Aix-en-Provence, France. Samples were collected during six successive crops (1997/1998–2002/2003). There exist, today, five French RDOs, including four that received an European protected designation of origin (PDO) (Fig. 1). Certain samples which come from RDOs 'Aix-en-Provence', 'Haute-Provence' and 'Nice' were analysed before the creation date of RDO but possess varietal compositions that make up the RDOs.

Table 1 shows the date of the creation of the RDOs, their registration as PDOs and the different constituted varieties. The RDOs are made up of primary and secondary varieties, as well as local and old varieties. 'Nyons' ($n = 126$), 'Haute-Provence' ($n = 85$) and 'Nice' ($n = 131$) are made up of one unique principal variety. 'Aix-en-Provence' ($n = 99$), and 'Vallée des Baux de Provence' ($n = 98$) have up to three or four principal varieties of which at least two do not have varietal proportions specified (Table 1).

2.2. Sensory characterisation

The fruity, bitter and pungent intensities were evaluated with the European method (EC Regulation, 2002). The oils coming from three olive harvests (2000, 2001, 2002) were tasted 2 and 14 months after their elaboration date. During this 12 month period, the samples were stored at 12 °C.

2.3. Chemical characterisation

2.3.1. Fatty acid determination

Olive oil in *n*-heptane (0.1 g/2 ml) was transmethylated with a cold solution of KOH (2M) according to the European Standard NF EN ISO 5509 (2000). Fatty acid methyl esters (FAME) were analyzed according to the European Standard NF EN ISO 5508 (1995). Analyses were performed on a Perkin–Elmer Autosystem 9000 gas chromatograph (GC) equipped with a split/split-less injector ($t = 250$ °C) and flame ionisation detector (FID) ($t = 250$ °C). A silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) coated with DB WAX (polyethylene glycol, JW) was used. The inlet pressure of the hydrogen as carrier gas was 154 kPa with a ratio: 70. The oven temperature program was as follows: 13 min at 200 °C, from 200 to 230 °C at 6 °C/min, 17 min at 230 °C.

2.3.2. Triacylglycerol determination

Triacylglycerols were analyzed by a HPLC system composed of a Merck liquid chromatograph Model

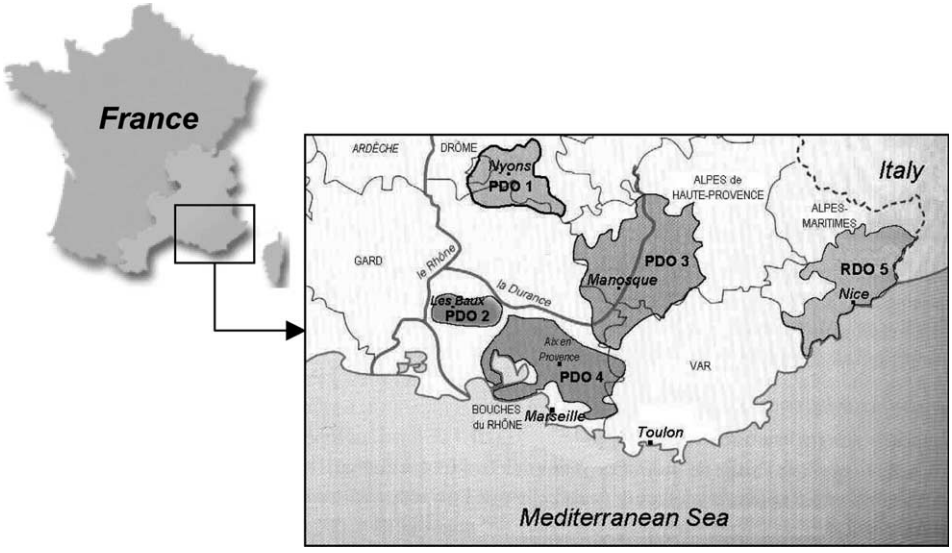

Fig. 1. Geographical areas of the five French RDOs. PDO1: Nyons; PDO 2: Vallée des Baux de Provence; PDO 3: Haute-Provence; PDO 4: Aix-en-Provence; RDO 5: Nice.

Table 1
Virgin olive oils from five French designation of origin

	Nyons (T)	Vallée des Baux (VB)	Aix-en-Provence (PA)	Haute Provence (A)	Nice (N)
Creation date of RDO	1994	1997	1999	1999	2001 and 2004
Registration date as PDO	1996	2000	2001	2001	No for moment
Primary varieties	Tanche	Agalandau[a], Grossane, Salonenque, Verdale BdR[b]	Aglandau, Cayanne, Salonenque	Aglandau	Cailletier
Secondary varieties	–	Picholine	Bouteillan, Grossane, Picholine, Verdale BdR[b]	Bouteillan, Picholine, Tanche	–
Local and old varieties	–	Yes	Ribiére, Sabine, Saurine, Sigoise, Triparde	Boube, Colombale, Estoublaisse, Filayre, Grapié	Araban, Blanquetier, Blavet, Nostral, Ribeyrou

[a] Synonym of Bégurette.
[b] Verdale des Bouches du Rhône.

LaChrom equipped with a Merck RP-18 Supersphere 100 column (250 × 4 mm i.d., 4 μm particle size, temperature 28 °C) coupled with a Merck refractometric L-7490 detector. A sample loop of 100 μl capacity was used in which 10 μl was injected. Acetone/acetonitrile, applying the IUCPA method, 2324 (1987) and propionitrile (Fiebig, 1985; Schulte, 1981) (Carlo Erba, Milan) were the mobile phases with a flow rate linear gradient (0.5–1 ml/min) for 47 min. Triacylglycerols in olive oils were separated according to equivalent carbon number (ECN), defined as CN-2*n*, where CN is the total acyl carbon number and *n* is the number of double bonds of fatty acids. Triacylglycerol identification was carried out with the help of standards and by comparing data from the literature (Fiebig, 1985; Moreda, Pérez-Camino, & Cert, 2003). POS and POA (e.g., in 2.5) triacylglycerols were identified after HPLC collection and FAME GC analysis.

2.4. Chemometric methods

The discrimination of the five oil origins was investigated by means of the linear discriminant analysis (Rencher, 1995). It is a multivariate statistical method designed for classifying a set of observations in predetermined classes. It makes it possible to investigate differences between the distributions of the fatty acid descriptors and the triacylglycerol contents in oil origin groups. For *k* groups, *k* linear combinations of variables are constructed, called discriminant functions. The calculation of the values of these functions for each sample makes it possible to allocate this sample

to the group for which the probability of belonging is the highest.

A method of cross-validation (leaving-one-out cross-validation) was performed for classifying the oil samples after the discriminant functions were estimated from all the others. The importance of each fatty acid and each triacylglycerol in discrimination, in the presence of the other contents, was investigated by analysing their coefficients in the discriminant functions. To make the comparisons more informative (Rencher, 1995), each coefficient in discriminant functions were multiplied by the standard deviation within groups of the related variable. Graphic representations were performed using the canonical variables. These synthetic variables are non-correlated linear combinations of initial variables (fatty acids and triacylglycerols) and are determined so that the rate of the variance between groups to the variance intra-groups are maximised. Plots of the samples on the plane defined by the two canonical variables make it possible to visualise the differences between the groups. Moreover, the linear correlation coefficients of fatty acid and triacylglycerol contents, with canonical variables, were calculated and represented on correlation circles. Each content is represented on these circles by a vector with components equal to the linear correlation coefficient with two canonical variables. These correlations show the contribution of each variable to the discrimination as it was alone and not in the presence of the others. They make it possible to characterise the different groups. The statistical analysis was performed with SAS system (SAS Institute, Inc., 1990) and especially with the discrim procedure for discriminant analysis.

2.5. Nomenclature

Fatty acids. 14:0, myristic acid (tetradecanoic acid); 16:0, palmitic acid (hexadecanoic acid); 16:1$n-9$, hypogeic acid (7-hexadecenoic acid); 16:1$n-7$, palmitoleic acid (9-hexadecenoic acid); 17:0, margaric acid (heptadecanoic acid); 17:1$n-8$, margaroleic acid (9-heptadecenoic acid); 18:1$n-9$, oleic acid (9-octadecenoic acid); 18:1$n-7$, *cis*-vaccenic acid (11-octadecenoic acid); 18:2$n-6$, linoleic acid (9,12-octadecadienoic acid); 18:3$n-3$, linolenic acid (9,12,15-octadecatrienoic acid); 20:0, arachidic acid (eicosanoic acid); 20:1$n-9$, gondoic acid (11-eicosenoic acid) (Ollivier et al., 2003); 22:0, behenic acid (docosanoic acid); 24:0, lignoceric acid (tetracosanoic acid).

Triacylglycerols. The triacylglycerols (TAG) are designated by letters corresponding to abbreviated names of fatty acid carbon chains that are fixed on the glycerol. The abbreviations of fatty acids names are: P, palmitoyl; Po, palmitoleyl; S, stearoyl; O, oleoyl; L, linoleoyl; Ln, linoleolenyl; and A, arachidoyl.

For the remainder of this study, the five RDOs will be designated by the following simplified names: Aix-en-Provence (PA), Haute-Provence (A), Nyons (T), Nice (C), and Vallée des Baux de Provence (Vallée des Baux, VB).

3. Results and discussion

Figs. 2–4 show the defining intervals of the medians (median: the 50th percentile of a distribution of numbers arranged in increasing order) for the three positive descriptors: fruity, bitter and pungent (EC Regulation, 2002). The intensities of these three attributes vary from one harvest to another. The intervals are defined by the averages of the lowest and highest limits of the confidence intervals, obtained from 10 to 17 samples from each designation. PA and A are fruitier than the three other RDOs, which are similar; PA has the highest bitterness level while T has the lowest. The RDOs are very close in pungency, except for T which has a much lower rate. The low bitterness and pungency levels for T is due to the fact that the oil is prepared with very ripe olives. A lowering of the intensity of the three descriptors is observed after a period of 12 months. The defining intervals are rather large then, especially for pungency which diminishes very quickly during conservation.

Fruity, bitter and pungent descriptors are not sufficient to take into account the sensory characteristics presented by these oils. The tasters identify each of the designations essentially through the fruitiness of each

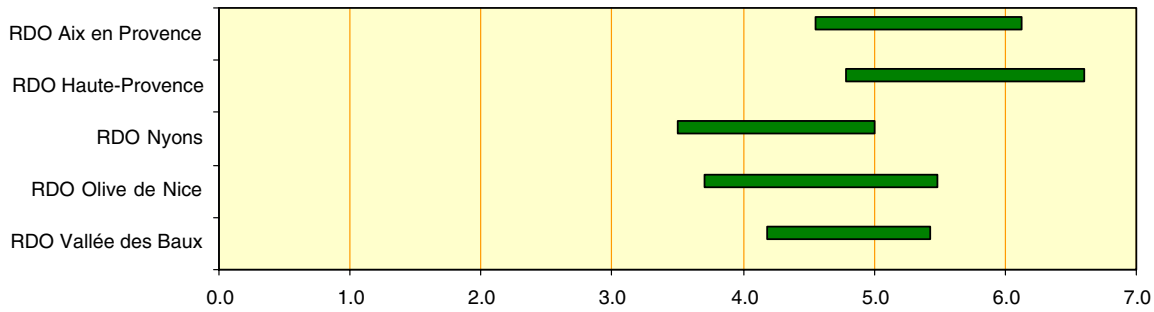

Fig. 2. Defining intervals of the medians for the fruitiness of the virgin olive oil of the five French RDOs.

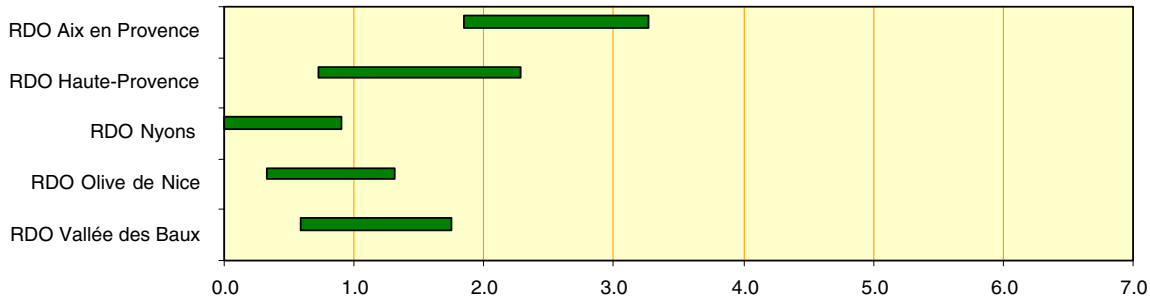

Fig. 3. Defining intervals of the medians for the bitterness of the virgin olive oil of the five French RDOs.

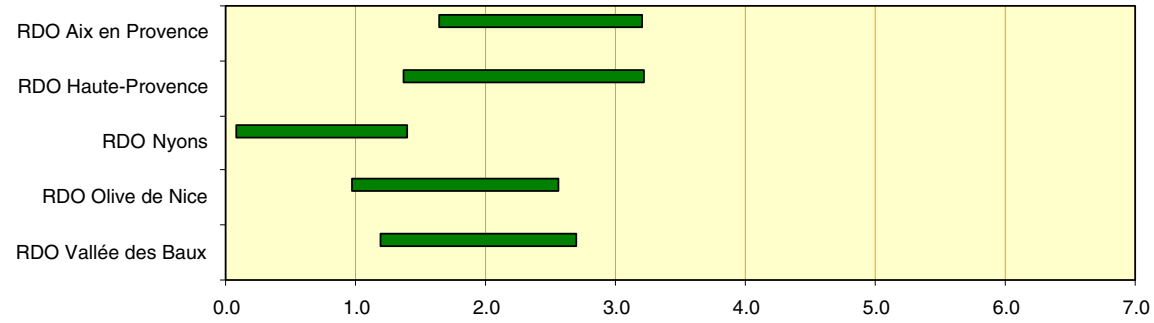

Fig. 4. Defining intervals of the medians for the pungency of the virgin olive oil of the five French RDOs.

RDO. The first three "fruity" analogical descriptors, the most often cited by the tasters, are shown in Table 2. These descriptors characterise each of five RDOs.

The oleic (18:1$n-9$), palmitic (16:0), linoleic (18:2$n-6$) and stearic (18:0) acids are the main fatty acids commonly found in virgin olive oils. The palmitoleic (16:1$n-7$), hypogeic (16:1$n-9$), oleic (18:1$n-9$) and *cis*-vaccenic (18:1$n-7$) acids are analysed separately contrary to European regulation (EEC Regulation, 1991) and to Codex Alimentarius (Codex Alimentarius, 2003) which count them together (Table 3). The fatty acids which leave slight traces (<0.01%) are not taken into account. All the values of fatty acids are in conformity to those of the International Olive Oil Council's regulation (IOOC, 2003) and Codex Alimentarius (Codex Alimentarius, 2003) with the exception of A where 72 samples out of 86 show a level of margaroleic acid (17:1$n-8$) higher than 0.3%. These results should be compared to those obtained for the variety Aglandau (Ollivier et al., 2003) which is the most important cultivar of A (Table 1). The European regulation (EEC Regulation, 1991) does not define the maximum value for this fatty acid.

T and C are the most unsaturated oils with ratios (MUFA + PUFA/SFA) (Table 3) of average values at 7.51 and 7.05, respectively. The least unsaturated oils are PA and VB with ratios at 4.92 and 4.89, respectively. A has an unsaturation average of 5.76.

PA and VB are the most saturated and polyunsaturated oils and the least monounsaturated, which is the opposite for T and C. These results illustrate the kinetic differences of reactions during the biosynthetic cascade of the fatty acids: palmitic, oleic and linoleic acids.

The analysis of the triacylglycerols by high-performance liquid chromatography (HPLC) was standardised in 1987 (IUPAC, 1987) and became the object of an European regulation (EC Regulation, 1997). This technique's over all principle is to use a reverse phase stationary phase, and as mobile phase, a mixture of acetone/acetonitrile. However, the obtained separation is not very satisfactory. For the past few years (Ollivier, Bruckert, Noyer, Guérère, & Artaud, 1999; Ollivier, Souillol, Noyer, Guérère, & Artaud, 2001), we have been using propionitrile (Fiebig, 1985; Schulte, 1981) as the elution solvent instead of the solvent mixture acetone/acetonitrile. The utilisation of propionitrile as the

Table 2
The principal analogical descriptors of the fruitiness of the five RODs

RODs	First descriptor	Second descriptor	Third descriptor
Aix en Provence	Artichoke	Fresh almond	Grass, leaf tomato bush
Haute-Provence	Artichoke	Banana	Pear, Fresh almond
Nyons	Green apple	Fresh hazelnut	Peach, Fresh almond
Nice	Fresh almond	broom flower	Artichoke
Vallée des Baux	Artichoke	Green pepper	Fresh hazelnut, Fresh almond

Table 3
Fatty acid composition (%) of 539 virgin olive oil samples[a] resulting from the five French RDOs

RDO	Aix-en-Provence (PA)			Haute-Provence (A)			Nyons (T)			Nice (C)			Vallée des Baux (VB)		
Samples no.	99			85			126			131			98		
Fatty acid	Mean (%)	Range		Mean (%)	Range		Mean (%)	Range		Mean (%)	Range		Mean (%)	Range	
		Min	Max		Min	Max		Min	Max		Min	Max		Min	Max
16:0	13.55	11.18	15.79	11.62	10.10	12.92	8.49	7.47	10.21	10.55	8.76	12.58	13.72	11.28	16.23
16:1$n-9$	0.13	0.11	0.17	0.14	0.09	0.16	0.15	0.11	0.19	0.11	0.06	0.19	0.13	0.10	0.15
16:1$n-7$	1.03	0.63	1.40	0.86	0.71	1.14	0.40	0.30	0.54	0.58	0.33	0.95	1.11	0.73	1.63
17:0	0.12	0.05	0.20	0.19	0.12	0.26	0.05	0.03	0.06	0.05	0.03	0.09	0.09	0.04	0.20
17:1$n-8$	0.22	0.08	0.37	0.38	0.25	0.53	0.08	0.06	0.10	0.10	0.07	0.18	0.16	0.09	0.36
18:0	2.59	2.17	2.99	2.42	2.22	2.69	2.69	2.38	3.04	2.11	1.64	2.92	2.55	2.02	3.01
18:1$n-9$	68.33	62.21	73.99	73.86	70.86	75.93	79.39	76.16	80.97	76.20	71.26	80.39	66.36	59.93	73.18
18:1$n-7$	2.39	1.80	2.95	2.26	1.94	2.63	1.47	1.16	1.76	2.01	0.72	2.71	2.51	2.10	3.09
18:2$n-6$	10.13	6.51	14.48	6.82	5.72	8.67	5.82	5.00	6.80	6.81	5.47	9.80	11.85	7.56	15.53
18:3$n-3$	0.63	0.52	0.82	0.61	0.51	0.78	0.62	0.52	0.76	0.63	0.46	0.96	0.65	0.55	0.77
20:0	0.43	0.36	0.49	0.40	0.34	0.46	0.38	0.34	0.43	0.37	0.29	0.44	0.43	0.38	0.48
20:1$n-9$	0.26	0.22	0.33	0.27	0.21	0.30	0.31	0.27	0.36	0.32	0.24	0.40	0.26	0.23	0.35
22:0	0.13	0.10	0.15	0.12	0.07	0.14	0.10	0.03	0.12	0.12	0.03	0.16	0.13	0.10	0.15
24:0	0.06	0.05	0.07	0.05	0.02	0.07	0.04	0.02	0.06	0.05	0.02	0.07	0.06	0.05	0.08
Squalene[b]	0.74	0.55	0.94	0.82	0.33	1.00	0.86	0.38	1.14	0.45	0.28	0.62	0.72	0.52	0.90
SFA	16.88	14.26	19.40	14.79	13.22	16.32	11.75	10.40	13.44	13.25	11.51	15.53	16.99	14.31	19.50
MUFA	72.36	66.80	77.74	77.76	74.74	79.37	81.80	79.01	83.17	79.32	75.05	83.01	70.51	64.61	77.19
PUFA	10.76	7.15	15.06	7.43	6.29	9.33	6.44	5.58	7.50	7.44	6.09	10.38	12.50	8.26	16.17

[a] Crops: 1997/1998, 1998/1999, 1999/2000, 2000/2001, 2001/2002, 2002/2003, values were calculated as the % of the total fatty acids.
[b] values were determined as the % of the total fatty acids and squalene sum, SFA saturated fatty acids sum, MUFA monounsaturated fatty acids sum, PUFA polyunsaturated fatty acids sum.

elution solvent allows us to improve the separation of the triacylglycerols which have been eluted or poorly resolved in the standard method as, for example, the crucial pairs LOO + PLnP/PoOO, PLO + SLL/PoOP, SOL/POO. Nevertheless, some triacylglycerols are not still separated. Propionitrile has the advantage of leading to a better chromatographic stability compared to the mixture acetone/acetonitrile. Similar results were obtained recently on the Chamlali and Picual varieties of virgin olive oil (Moreda et al., 2003). Fig. 5 shows the improvement of the separations of the triacylglycerols from the same virgin olive oil using propionitrile as the eluent compared to the official method using the mixture acetone/acetonitrile.

Table 4 gives variation ranges and the average value for triacylglycerols from those olive oils whose harvests were studied during six-years. The oils of the five RDOs are characterised by four primary triacylglycerols: OOO, POO, LOO and PLO and three secondary triacylglycerols: LOL, POP and SOO. For all the RDOs, OOO makes up the biggest part with levels that vary. Thus, T (54.59%) and C (49.01%) have the highest level of OOO while PA (35.81%) and VB (32.63%) have the lowest level. A (45.36%) has an intermediate level. These results agree with those found for the fatty acids. Because of the variability in fatty acid and triacylglycerol compositions in the RDO samples, multivariate statistical methods were performed to describe the RDO characteristics. The discrimination between the five groups was investigated by means of the linear discriminant analysis method. Each oil sample was described by 37 relative percentages of individual acids, SFA, MUFA, PUFA, triacylglycerols and squalene variables. The Mahalanobis distances between the RDOs are shown in Table 5.

The two closest origins (Mahalanobis $D^2 = 19.60$) were PA and VB. The T oil was the most removed from the others with C being its closest neighbor (Mahalanobis $D^2 = 115.63$). Because there are five groups, only four discriminant functions can be calculated.

The representation of the samples in terms of the canonical variables clearly shows the relative positions of five groups (Figs. 6–8) and their identicalness. The correlation circles display on each coordinate the correlation coefficients of the canonical variables with fatty acids and triacylglycerols. According to the standardised discriminant coefficient, the most important variables for discriminating between groups in a multivariate context are, in descending order: OOO, LOO, POO, PoOO, LOL, MUFA, oleic, palmitic, stearic and hypogeic acids. However, it must be noted that all the variables are useful for discrimination. The most important variables for characterising the groups are also those which give the strongest standardised discriminant coefficient (Rencher, 1995). We note three groups of samples concerning the two first canonical variables (Fig. 6). The first canonical variable gives a separation between, on one hand, T and C groups and on the other hand, A, PA and VB. The second canonical variable shows a

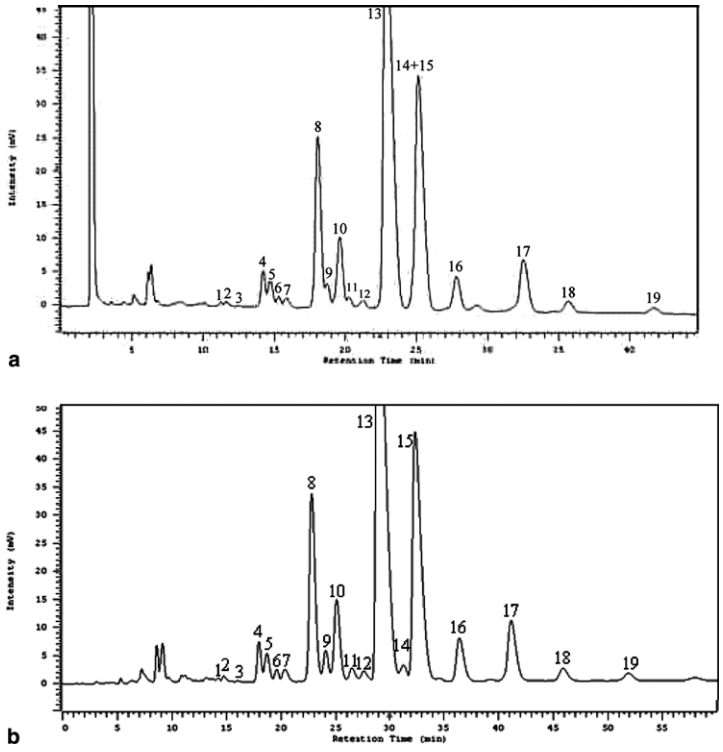

Fig. 5. HPLC separations of one virgin olive oil with acetone/acetonitrile (a) and propionitrile (b) as eluents. (1) LLL; (2) OLLn + PoLL; (3) PLLn; (4) OLL; (5) OOLn; (6) PLL; (7) POLn; (8) LOO + PLnP; (9) PoOO; (10) PLO + SLL; (11) PoOP; (12) PLP; (13) OOO; (14) SOL; (15) POO; (16) POP; (17) SOO; (18) POS; (19) POA.

Table 4
Triglycerides composition (%) of 539 virgin olive oil samples[a] resulting from the five French RDOs

RDO	Aix-en-Provence (PA)			Haute-Provence (A)			Nyons (T)			Nice (C)			Vallée des Baux (VB)		
Samples no.	99			85			126			131			98		
triacylglycerol	Mean (%)	Range		Mean (%)	Range		Mean (%)	Range		Mean (%)	Range		Mean (%)	Range	
		Min	Max		Min	Max		Min	Max		Min	Max		Min	Max
LLL	0.21	0.06	0.47	0.08	0.03	0.16	0.06	0.02	0.13	0.06	0.01	0.15	0.31	0.11	0.67
OLLn + PoLL[b]	0.32	0.19	0.53	0.18	0.11	0.35	0.17	0.10	0.24	0.20	0.13	0.36	0.39	0.24	0.64
PLLn	0.09	0.04	0.14	0.04	0.02	0.10	0.02	0.00	0.08	0.05	0.02	0.07	0.11	0.06	0.19
LOL	2.91	1.36	4.98	1.29	0.61	2.03	1.13	0.57	1.70	1.30	0.57	2.38	3.80	1.78	5.65
OOLn	1.65	1.03	2.02	1.41	0.74	1.95	1.47	0.83	2.03	1.40	0.64	2.26	1.80	1.45	2.01
PLL	1.09	0.44	2.20	0.39	0.11	0.67	0.17	0.05	0.37	0.35	0.10	0.82	1.53	0.60	2.75
POLn	0.84	0.67	1.11	0.74	0.51	0.95	0.46	0.25	0.72	0.60	0.32	1.00	0.91	0.63	1.12
LOO + PLn P[b]	14.97	11.52	18.13	12.05	10.22	14.54	12.00	10.29	13.87	12.83	10.39	16.68	16.35	12.16	18.70
PoOO	1.88	1.27	2.31	1.55	0.70	2.27	0.78	0.27	1.27	1.04	0.20	2.01	2.06	1.65	3.21
PLO + SLL[b]	7.74	4.94	10.58	4.90	3.51	6.31	3.14	2.16	4.10	4.61	3.30	6.97	9.04	5.70	11.56
PoOP	0.93	0.47	1.32	1.09	0.77	1.37	0.27	0.17	0.39	0.46	0.24	0.87	1.01	0.63	1.63
PLP	0.80	0.40	1.32	0.34	0.17	0.66	0.17	0.00	0.27	0.29	0.00	0.69	1.07	0.47	1.59
OOO	35.81	27.71	45.01	45.36	39.71	51.94	54.59	50.95	58.58	49.01	40.43	56.02	32.63	25.22	42.68
SOL	1.03	0.58	1.56	0.58	0.07	1.02	0.62	0.11	1.06	0.46	0.04	0.93	1.17	0.61	1.61
POO	21.72	18.70	24.56	21.69	18.95	24.92	17.22	14.69	18.78	20.15	17.56	22.92	19.80	17.03	23.47
POP	3.56	2.41	4.40	3.31	2.53	4.64	2.03	1.53	2.65	2.69	1.99	3.95	3.49	2.89	4.06
SOO	3.18	2.53	3.96	3.70	2.98	4.59	4.49	3.73	5.60	3.32	2.43	5.12	3.17	2.63	3.69
POS	0.86	0.59	1.21	0.83	0.60	1.24	0.68	0.38	1.05	0.66	0.43	1.19	0.89	0.59	1.34
POA	0.43	0.30	0.54	0.49	0.32	0.70	0.52	0.35	0.74	0.51	0.33	0.98	0.44	0.30	0.80

[a] Crops: 1997/1998, 1998/1999, 1999/2000, 2000/2001, 2001/2002, 2002/2003, values were calculated as the % of the total.
[b] Low-level triacylglycerol.

discrimination between C and the other groups. Concerning the first two canonical variables, A, PA and VB are practically the same.

The correlation circle (Fig. 7) shows that T is characterised by concentrations higher than the average in MUFA, OOO, SOO, squalene and stearic acid and is

Table 5
Mahalanobis' distances between the origin groups

		To				
		Haute-Provence (A)	Nice (C)	Aix-en-Provence (PA)	Nyons (T)	Vallée des Baux (VB)
From	Haute Provence (A)	0	114.49	42.62	133.35	71.57
	Nice (T)	114.49	0	89.84	115.63	107.10
	Aix-en-Provence (PA)	42.62	89.84	0	145.43	19.60
	Nyons (T)	133.35	115.63	145.83	0	148.66
	Vallée des Baux (VB)	71.57	107.10	19.60	148.66	0

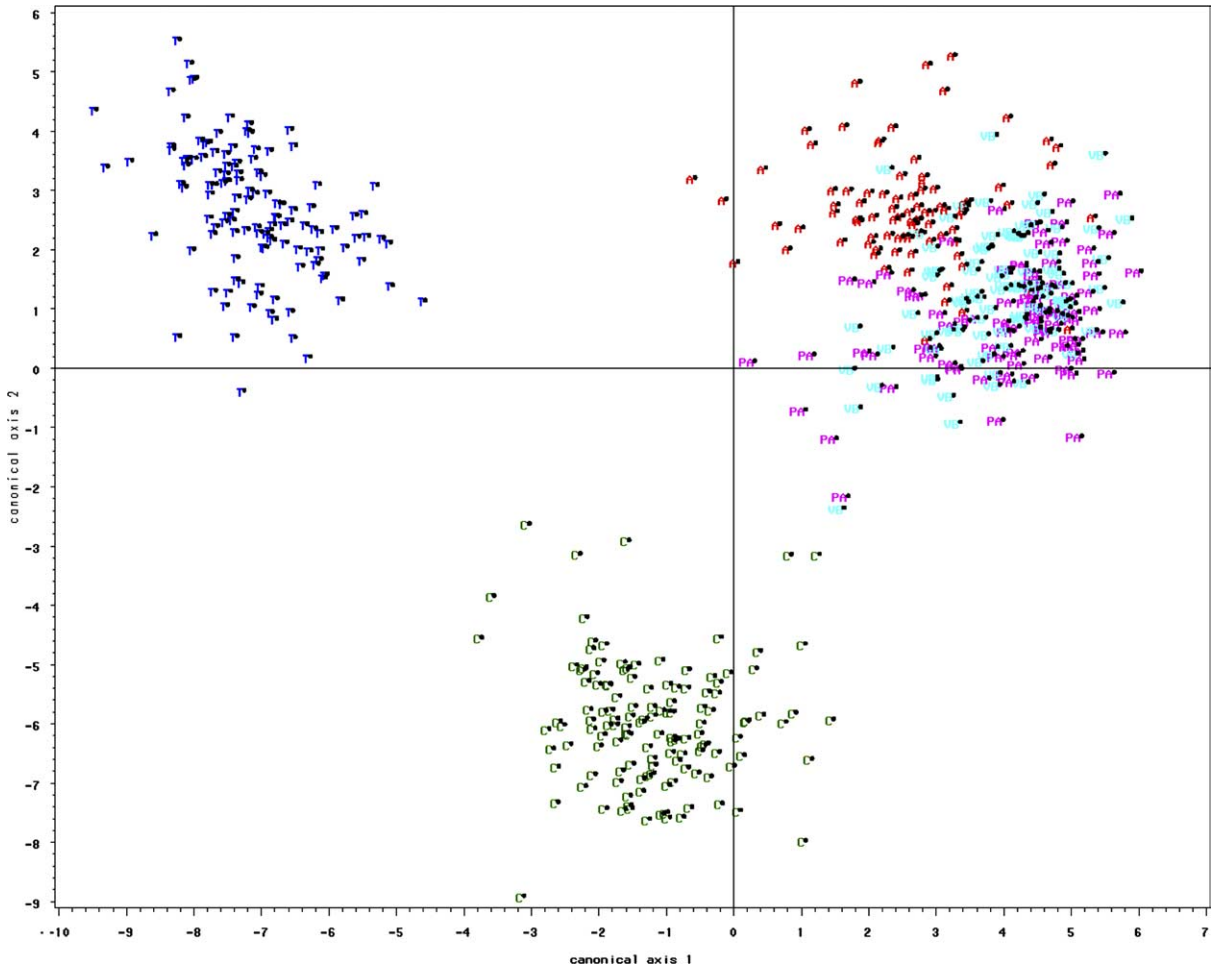

Fig. 6. Plan of the canonical axes 1 and 2 with Nyons (T), Nice (C), Haute-Provence (A), Aix-en-Provence (PA) and Vallée des Baux (VB) RODs.

characterised by concentrations lower than the average in *cis*-vaccenic acid, SFA, POO. C is essentially characterised by low concentrations of squalene, stearic, hypogeic acids; other concentrations are closer to mean values. A, PA and VB are essentially characterised by concentrations higher than mean values in *cis*-vaccenic acid, PoOP, arachidic acid and low concentrations in MUFA, gondoic acid and OOO.

The canonical variable 3 (Fig. 8) discriminates between A on one hand and PA, and VB on the other hand. A is characterised by higher concentrations in margaroleic and margaric acids and lower concentrations in LOO, LOL, LLL, than VB. PA is at an intermediary position between the two preceding groups, close to VB.

The canonical variable 4 shows a difference between PA and VB (Fig. 9). The coefficients of the correlation of the variables with the canonical variable 4 are weak. However, if we take as a basis the standardised discriminate coefficients, we can explain that the existing differences between the PA and VB groups are due to the distances in the level of the following variables: OOO, PLO, MUFA, linoleic and margaroleic acids.

We obtained the results displayed in Table 6 using a cross-validation method for classifying the samples. The

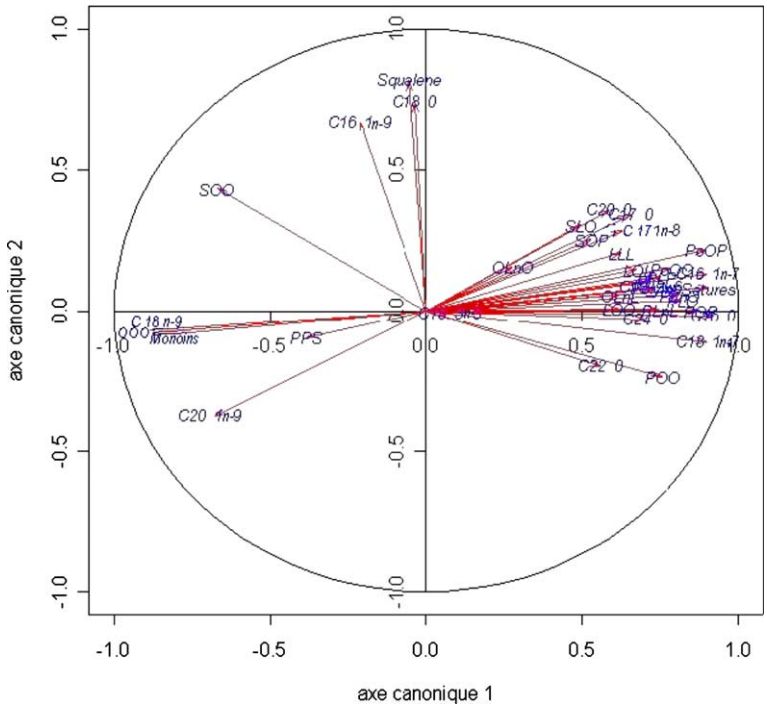

Fig. 7. Correlation circle of the coefficients of correlation of all variables with the canonical variables 1 and 2.

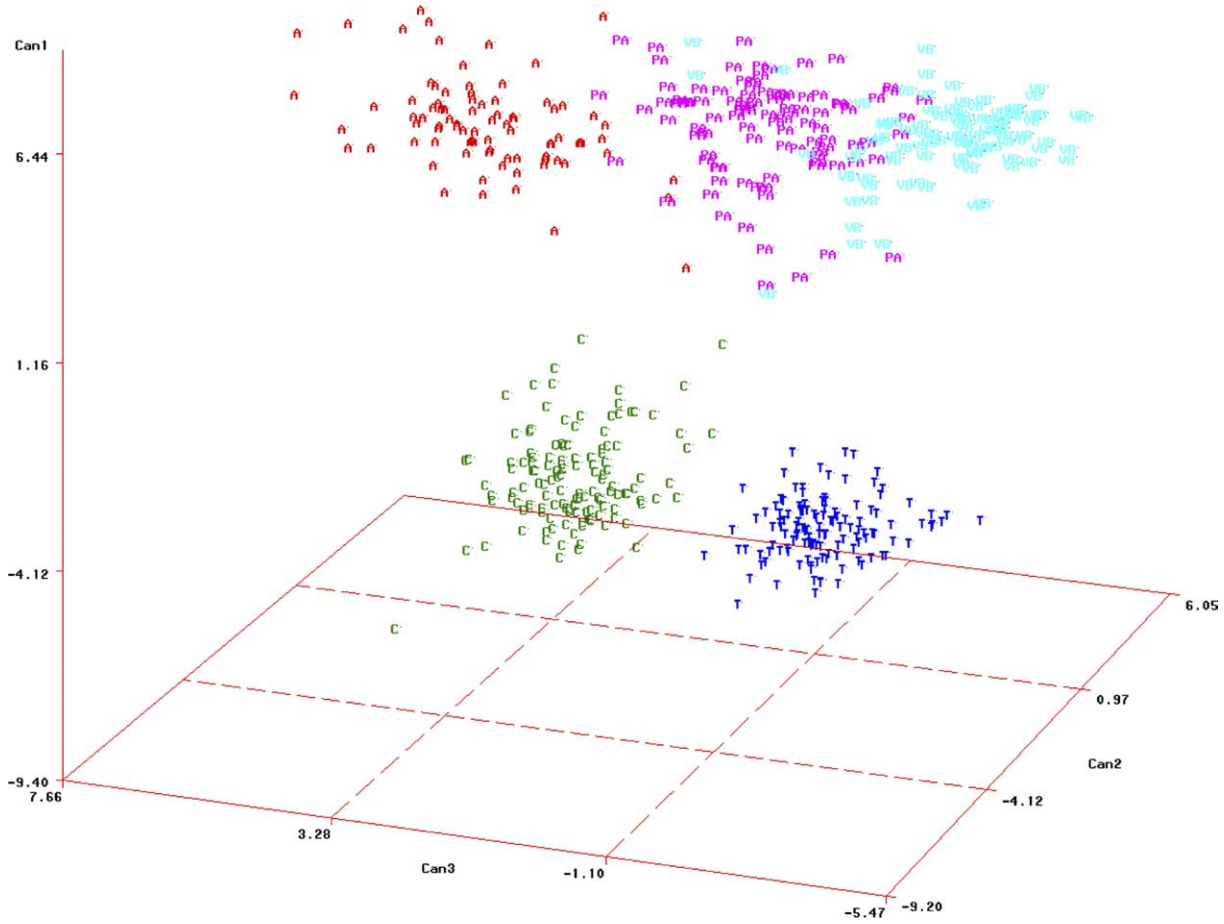

Fig. 8. Representation of the samples in the sub-spaces of the first three canonical variables.

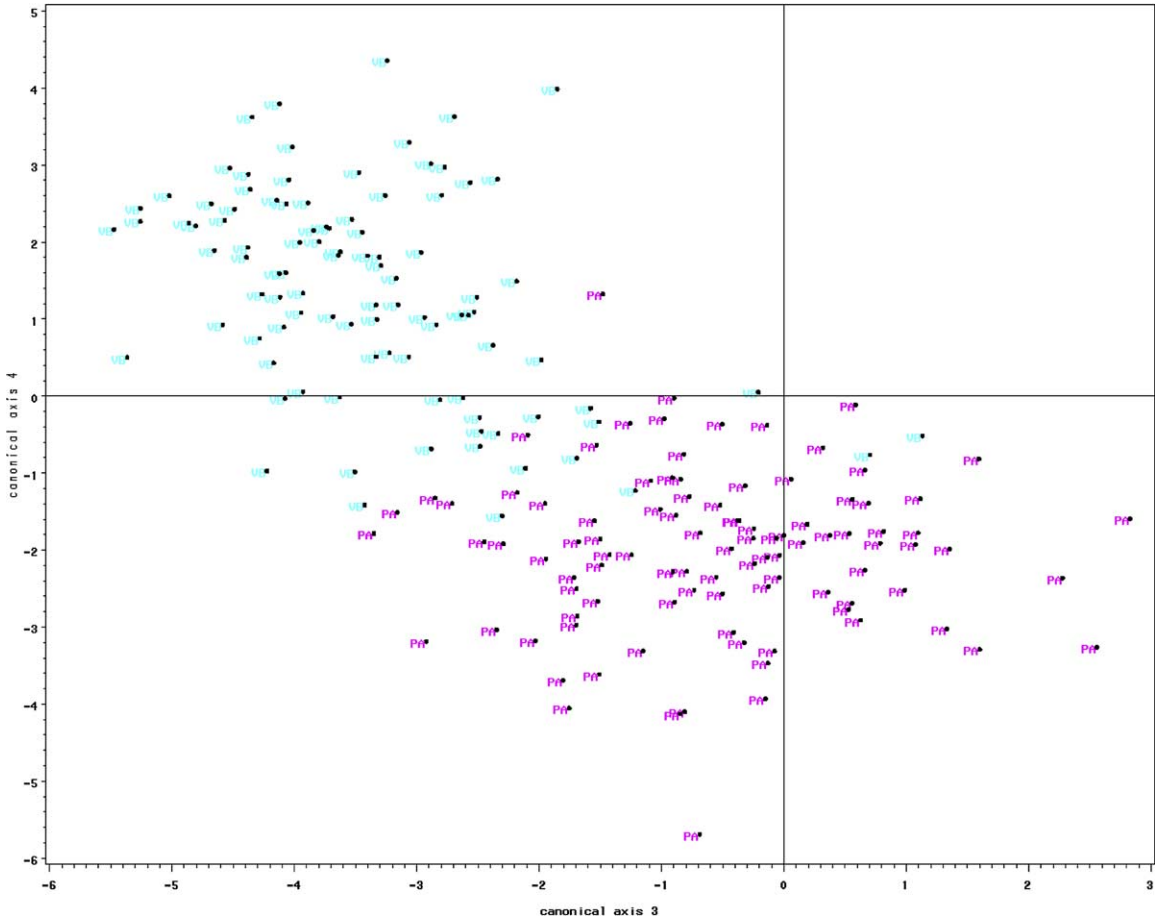

Fig. 9. Plan of the canonical axes 3 and 4 with Aix-en-Provence (PA) and Vallée des Baux (VB) RODs.

Table 6
Classification of oil samples according to their origin

		To					
		Haute-Provence (A)	Nice (C)	Aix-en-Provence (PA)	Nyons (T)	Vallée des Baux (VB)	Total
From	Haute-Provence (A)	84	0	1	0	0	85
	Nice (C)	0	131	0	0	0	131
	Aix-en-Provence (PA)	1	0	95	0	3	99
	Nyons (T)	0	0	0	126	0	126
	Vallée des Baux (VB)	0	0	14	0	84	98

mean error rate is about 4%. Indeed, the error rates are zero or very low except for the VB group (14.3%). All T and C samples are correctly classified. Only one A sample is classified in the PA group by the method. Four PA samples are misclassified. Three PA samples are identified as VB group and one is identified as A group. Fourteen VB samples are classified in the PA group. PA and VB RDOs are poly-varietal oils and are made up, among other components, of the two principal cultivars: Salonenque and Aglandau (Table 1). The varietal compositions of these two RDOs is close, which explains the difficulties in completely separating them. As a general rule, during blending, the cultivar Salonenque is the dominant factor in the VB oils while the cultivar Aglandau is dominant in the PA oils. The statistical study confirms that these two varieties are the dominant ones for each of the two RDOs.

Acknowledgements

This study has been carried out with financial support from the Commission of the European Communities, specific RTD programme "Quality of Life and Management of Living Resources", QLK1-CT-2002-02386, "Traceability of origin and authenticity of olive oil by

combined genomic and metabolomic approaches (OLIV-TRACK)". The authors appreciate the technical assistance of Muriel Richard and Frédérique Franceschi.

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