Authentication of European Virgin Olive Oils by Their Chemical Compounds, Sensory Attributes, and Consumers' Attitudes

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Twenty-four samples of four European virgin olive oil varieties—Arbequina, Coratina, Koroneiki, and Picual, cultivated in Greece, Italy, and Spain—have been analyzed from their chemical composition (either nonvolatile compounds (31)—fatty acids, sterols, alcohols, and methylsterols—or volatile ones (65)—aldehydes, alcohols, furans, hydrocarbons, acids, ketones, and esters), sensory attributes (103), and consumers' attitudes, the latter in terms of their overall acceptability and sensory comments from their acceptability trials. The paper describes and explains the most remarkable of these parameters characterizing the virgin olive oil varieties, which can be useful in virgin olive oil authentication. The agreement between the concentration of chemical compounds and sensory attributes is explained wherever possible.

Keywords: *Virgin olive oil; authenticity; flavor; analysis; consumers' attitudes*

INTRODUCTION

The criteria that define the authenticity or genuineness of a food product are numerous and vary from one foodstuff to another. In the case of virgin olive oil, authenticity issues may be associated with a given geographical origin, method of processing, or variety (Lees, 1995). However, standards, either in national or in European Communities legislation, by which the authenticity of virgin olive oil can be judged, should take into account not only its chemical composition but also its genuine sensory attributes.

In the last few years there has been great interest in virgin olive oil authentication either by statistical procedures (Aparicio and Albi, 1987; Aparicio *et al*., 1991a,b; Tsimidou and Karakostas, 1993; Baeten *et al*., 1996) or beyond these (Aparicio, 1988; Aparicio and Alonso, 1994; Aparicio et al., 1994a). However, only a few papers have been published concerning quality authentication (Solinas *et al*., 1987; Morales and Aparicio, 1993; Morales *et al*., 1994), though none of them by sensory profilings. Perhaps researchers have avoided sensory authentication because of the complex evaluation of attributes and the great number of them perceived for virgin olive oil (Aparicio *et al*., 1994b). In fact, in the authentication of a foodstuff by its sensory attributes, the doubt always remains whether authentication carried out by other assessors would reach similar conclusions. On the basis of such doubt, virgin olive oils should be authenticated under the widest conditions in order to minimize the possibility that conclusions could be attained by chance or be influenced by olive oil characteristics or assessors' habits (Aparicio *et al*., 1994b; Aparicio and Morales, 1995).

When chemical compounds and sensory attributes are analyzed in virgin olive oils, the possible differences between them are basically due to olive variety. The importance of olive variety in authentication arises from the biochemical pathways producing the chemical compounds quantified in virgin olive oil. In consequence, the olive variety is basic for determining the inherent sensory quality of its virgin olive oil, its characterization, and, hence, its authentication.

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Table 1. Nonvolatile Chemical Compounds Quantified and Identified in the Samples

code	chemical compd	code	chemical compd
1	palmitic acid	17	taraxerol
2	palmitoleic acid	18	dammaradienol
3	margaric acid	19	β-amyrin
4	margaroleic acid	20	butyrospermol
5	stearic acid	21	24-methylene-24-dihydrolanosterol
6	oleic acid	22	cycloarthenol
7	linoleic acid	23	24-methylenecycloarthanol
8	linolenic acid	24	campesterol
9	arachidic acid	25	stigmasterol
10	gadoleic acid	26	β-sitosterol
11	phytol	27	Δ^5-avenasterol
12	erythrodiol	28	obtusifoliol
13	docosanol	29	gramisterol
14	tetracosanol	30	cycloeucalenol
15	hexacosanol	31	citrostadienol
16	octacosanol		

This paper studies the sensory and chemical authentication of the most marketed virgin olive oil varieties—Arbequina, Picual, Coratina, and Koroneiki—(Morettini, 1950; Hermoso *et al*., 1991). Thirty-one nonvolatile compounds (fatty acids, sterols, alcohols, methylsterols) and 65 volatile ones (aldehydes, alcohols, furans, hydrocarbons, acids, ketones, esters) have been used to show that virgin olive oil authentication is closely related with the olive variety from which oil is obtained by strictly physical means. The sensory authentication has been carried out by assessors, both potential and habitual, of different nationalities, and the results agree with those from volatile compounds responsible for virgin olive oil aroma.

MATERIALS AND METHODS

Data Set. The data set was made up of 12 virgin olive (*Olea europea* L.) oil samples from fruit harvested in two different years ($n = 24$) and collected from Greece (Heraklion, Crete), Italy (Bitonto, Puglia), and Spain (Córdoba and Jaén, Andalusia). The varieties—Arbequina and Picual from Spain, Coratina from Italy, and Koroneiki from Greece—were selected because they are widely used in the bottled olive oil trade (Morettini, 1950; Hermoso et al., 1991). Fruits were picked, in perfect sanitary conditions, at three stages of ripeness: unripe, normal ripeness, and overripe (EOC, 1976). Oils were obtained, under the best conditions, using three extraction

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Table 2. Volatile Compounds Identified and Quantified in the Olive Oil Samples and Sensory Characterization of Volatiles by the Statistical Sensory Wheel

code[a]	chemical compd	concn[b]	sensory wheel[c]
1	methyl acetate	0.012	green
2	octene	0.011	green
3	ethyl acetate	0.042	undesirable
4	butan-2-one	0.003	fruity
5	3-methylbutanal	0.053	ripe fruit
6	1,3-hexadien-5-yne	0.014	green
7	an alcohol	0.059	fruity
8	ethylfuran	0.060	sweet-green
9	ethyl propanoate	0.052	sweet-green
10	an alcohol + hydrocarbon	0.212	ripe-undesirable
11	3-pentanone	tr	green
12	4-methylpentan-2-one	tr	green
13	pent-1-en-3-one	0.221	sweet
14	2-methylbut-2-enal	0.070	undesirable
15	a hydrocarbon	0.246	sweet-green
16	methylbenzene	tr	ripe fruit
17	2-methylbut-3-enol	0.005	undesirable
18	butyl acetate	0.106	sweet-green
19	hexanal	0.195	sweet
20	a hydrocarbon	0.150	sweet-green
21	2-methylbutylpropanoate	0.004	bitter
22	2-methyl-1-propanol	0.046	green
23	(*E*)-2-pentenal	0.015	green
24	an alcohol	0.011	undesirable
25	(*Z*)-2-pentenal	0.022	ripe-undesirable
26	ethylbenzene	0.080	bitter
27	(*E*)-3-hexenal	0.057	ripe fruit
28	(*Z*)-3-hexenal	0.365	green
29	1-penten-3-ol	0.237	undesirable
30	3-methylbutyl acetate	0.045	bitter
31	heptan-2-one	0.013	ripe fruit
32	(*Z*)-2-hexenal	0.050	green
33	(*E*)-2-hexenal	10.998	bitter
34	2-methylbutan-1-ol	0.021	ripe-undesirable
35	3-methyl butanol	0.002	undesirable
36	3-methyl-2-butenyl acetate	0.025	undesirable
37	dodecene	0.101	undesirable
38	pentan-1-ol	0.004	fruity
39	ethenylbenzene	0.019	fruity
40	hexyl acetate	0.180	green
41	a C_8 ketone	0.002	green
42	octan-2-one	0.008	ripe olives
43	3-(4-methyl-3-pentenyl) furan	0.057	ripe olives
44	3-hexenyl acetate	0.089	green
45	(*Z*)-2-penten-1-ol	0.576	green
46	6-methyl-5-hepten-2-one	0.027	bitter
47	nonan-2-one	0.029	sweet-green
48	hexan-1-ol	0.466	undesirable
49	(*E*)-3-hexen-1-ol	0.017	bitter
50	tridecene	0.167	bitter
51	(*Z*)-3-hexen-1-ol	0.606	green
52	2,4-hexadienal	0.002	ripe fruit
53	(*E*)-2-hexen-1-ol	0.662	undesirable
54	acetic acid	0.015	undesirable
55	methyl decanoate	0.024	green-bitter
56	hydrocarbon C_{11}	0.026	bitter
57	hydrocarbon	0.592	bitter-pungent
58	4-methyl-1-penten-3-ol	0.004	ripe fruit
59	1,2,4-trimethylbenzene	0.011	undesirable
60	2-methyl-4-pentenal	0.026	bitter-pungent
61	alcohol C_6 branched	0.005	ripe fruit
62	(*Z*)-2-hexen-1-ol	0.054	green
63	2-octenal	0.017	green
64	propanoic acid	0.044	green-bitter
65	hydrocarbon	0.209	green

[a] The codes identify the chemical compounds described in the paper. [b] Mean concentration in ppm. [c] The sector of the SSW where the chemical compound was located.

systems, centrifugation, percolation, and pressing and were freeze-stored until the moment of analysis.

Chemical Compounds. All the chemical compounds (Table 1) were measured by gas chromatography using different procedures.

Table 3. Basic Characteristics of the Panels That Carried Out the Sensory Evaluations

	group					
	A	B	C	D	E	F
nationality	Spanish	Italian	Greek	Italian	British	Dutch
no. of assessors	10	10	14	11	9	8
assessors' level[a]	F	T	T	F	T	T
consumer[b]	H	H	H	H	P	P
no. of attributes	15	14	14	10	13	59
scale[c]	S	S	S	S	U	U
scores	1−5	1−5	1−5	1−9	100 mm	130 mm

[a] F (full), T (trained for this work). [b] H (habitual), P (potential). [c] S (structured), U (unstructured).

Fatty acids were measured as their methyl esters produced by interesterification, neutralization, and subsequent methylation using a solution of HCl in methanol. A solution of water saturated with NaCl was then added, and the final solution was extracted with hexane. The organic phase was analyzed by a Perkin-Elmer Sigma 2000 gas chromatograph (EGS 2.5%, Chromosorb W80-100, 2 m × 2 mm). An equal response factor was considered for the whole set of fatty acids.

In order to quantify alcohols, sterols, and methylsterols, 2 mL of a solution of 0.25 mg/mL heneicosanol and 0.25 mg/mL betulin in isopropyl ether was added to 5 g of virgin olive oil. The chemical series were then determined by saponification of the oils and fractionation by thin-layer chromatography (Whatman, 20 × 20 cm, 250 mm layer) of the unsaponificable matter using *n*-hexane:ethyl acetate 85:15 (v/v) as developer. Three large bands were removed from the TLC plate. The first one contained triterpenic alcohols, a part of the phytol and aliphatic alcohols. The second one contained the rest of the phytol, and aliphatic alcohols, methylsterols, and hydroxy aldehyde-triterpene, and the third one contained sterols and erythrodiol. The three separated bands and the fractions recovered from them were extracted separately with isopropyl ether (10 mL). The solutions were silanized (150 μL) with a mixture of pyridine, hexamethyldisilane, and trimethylchlorosilane (9:3:1) though cholestane (2 mL of a solution 0.025 mg/mL in isopropyl ether) was previously added to the first and second bands.

A Hewlett-Packard HP-5890 gas chromatograph was fitted with a flame ionization detector (FID) and a split injection system. Separation was carried out on capillary columns (25 m × 0.3 mm) coated with methylphenylsilicone HP-5 of 0.17 μm thickness. In the case of alcohols and methylsterols the operating conditions were as follows: oven temperature, 250 °C for 1 min, subsequently increased at 0.6 °C/min to 280 °C; injector temperature, 275 °C, detector temperature, 300 °C; carrier gas, nitrogen. In the case of sterols, the initial oven temperature was 275 °C for 15 min, thereafter increasing at 1 °C/min to 285 °C.

The phytol and aliphatic alcohol contents were determined by adding the data of the first and second portions, using the cholestane peak as weight, and quantifying the results with heneicosanol.

Triterpenic alcohols and methylsterols were also quantified with heneicosanol, while sterols and erythrodiol were quantified with betulin.

Volatile compounds were analyzed with a dynamic headspace technique under determined optimized conditions as previously described (Morales et al., 1994). A 0.5 g olive oil sample was heated at 40 °C and swept with N_2 (200 mL/min) for 15 min. Tenax TA (Chrompack) was used as a trap. Volatiles were thermally desorbed at 220 °C onto a fused-silica trap cooled at −110 °C for 5 min just before injection, which was carried out by flash heating of the cold trap at 170 °C for 5 min. The volatiles were transferred onto a fused-silica Supelcowax 10 capillary column (60 m, 0.32 mm id, 0.5 μm film thickness). The oven temperature was held at 40 °C for 4 min and programmed to rise at 4 °C/min to a final temperature of 240 °C, where it was held for 10 min. A Hewlett-Packard 5890 series II with FID detector was employed. For quantitative analysis, isobutyl acetate was used as internal standard.

Table 4. Sensory Attributes Evaluated by the Panels with Different Methods of Perception

panel[a]	attribute[b]	perception[c]	code[d]	panel[a]	attribute[b]	perception[c]	code[d]	panel[a]	attribute[b]	perception[c]	code[d]
A	olive fruity (green)	flavor	1	E	strength of olive	odor	36	F	salty	taste	70
A	apple	flavor	2	E	strength of olive	flavor	37	F	olives	taste	71
A	other ripe fruits	flavor	3	E	banana skins	flavor	38	F	green leaf	taste	72
A	green	flavor	4	E	tomato	flavor	39	F	grass	taste	73
A	bitter	flavor	5	E	sweet	odor	40	F	green banana (not ripe)	taste	74
A	pungent	flavor	6	E	hay/composty	flavor	41	F	dried green herbes	taste	75
A	sweet	flavor	7	E	perfumey	odor	42	F	minced pepper	taste	76
A	rancid	odor	8	E	perfumey	flavor	43	F	red chili pepper	taste	77
A	olive fruity (ripe)	flavor	9	E	grassy	flavor	44	F	cream/butter	taste	78
B	olive fruity (ripe and green)	flavor	10	E	almond	flavor	45	F	coconut	taste	79
B	other ripe fruits	flavor	11	E	throatcatching	mouth feel	46	F	caramel	taste	80
B	green	flavor	12	E	thickness	mouth feel	47	F	grotty	taste	81
B	bitter	flavor	13	E	pungent	flavor	48	F	velvet like	mouth feel	82
B	pungent	flavor	14	F	odor intensity	odor	49	F	sticky	mouth feel	83
B	sweet	flavor	15	F	sea breeze on the beach	odor	50	F	slightly burned/ toasted	taste	84
B	allowable	flavor	16	F	prickling	odor	51	F	ash tray	taste	85
B	rough	aftermouth feel	17	F	apple	odor	52	F	glue with ethylacetate	taste	86
C	olive fruity (ripe and green)	flavor	18	F	twig	odor	53	F	refinery	taste	87
C	apple	flavor	19	F	pine/harshy	odor	54	F	bitter	taste	88
C	other ripe fruits	flavor	20	F	lemon	odor	55	F	astringent	mouth feel	89
C	green	flavor	21	F	orange	odor	56	F	green	aftertaste	90
C	bitter	flavor	22	F	soft fruits	odor	57	F	fruity	aftertaste	91
C	pungent	flavor	23	F	candies (fruit)	odor	58	F	cooling/ evaporating	aftermouth feel	92
C	sweet	flavor	24	F	wild flowers in springtime	odor	59	F	glue with ethylacetate	aftertaste	93
C	rough	aftermouth feel	25	F	fermenting fruit	odor	60	F	cocoa butter/ white chocolate	aftertaste	94
D	tomato	aroma	26	F	farm	odor	61	F	putty/linseed oil	aftertaste	95
D	ripe black olives	aroma	27	F	oil for salads (soybean oil)	odor	62	F	used frying oil	aftertaste	96
D	green olives	aroma	28	F	tallow	odor	63	F	trany	aftertaste	97
D	cut green grassy	aroma	29	F	cod liver oil	odor	64	F	dry wood	aftertaste	98
D	artichoke	aroma	30	F	nuts	odor	65	F	dusty	aftertaste	99
D	apple	aroma	31	F	medicine	odor	66	F	dry	aftermouth feel	100
D	yeast	aroma	32	F	earthy	odor	67	F	sharp/etching	aftermouth feel	101
D	bitter	taste	33	F	taste intensity	taste	68	F	pungent/ sharp throat	aftermouth feel	102
D	pungent	mouth feel	34	F	sweet	taste	69	F	rough	aftermouth feel	103
D	astringent	mouth feel	35								

[a] Panel types are described in Table 2. [b] Attributes evaluated by each panel. [c] Kind of perception used to evaluate the attributes. [d] The codes identify the attributes described in the paper.

Peaks were identified by mass spectral analyses by using an MS 30/70 VG mass spectrometer (VG Analytical, Manchester, U.K.) and a VG 11/250 data system. Operating conditions were as previously described (Morales et al., 1995). Sample components were verified by comparison of mass spectral data with those of authentic reference compounds. When standards were not available, sample components were tentatively identified by mass spectrum matching by using the NBS mass library collection. Table 2 shows the all volatiles used in this study and their approximate mean concentration in samples.

To assess the aroma notes corresponding to olive oil volatile compounds, a high-resolution gas chromatography (HRGC)-sniffing technique was applied to virgin olive oil samples of each variety (Morales et al., 1995). The effluent of GC column was split 1 to 10 to the detector and the sniffing port, respectively. The odor-active regions of the eluate were evaluated and their aroma notes assigned by five assessors—two with more than 10 years experience and three who, while not being experienced, were habitual consumers of virgin olive oil. The odor descriptions were noted on a form with a preprinted time scale; assessors did not see the chromatogram. Assessors basically agree on the odors of volatiles though different semantic terms were used to describe some of them. An open-minded discussion was held with assessors to decide the final sensory attributes; later these sensory attributes were clustered into the olive oil basic sensory attributes (Table 2) by the statistical sensory wheel (Aparicio et al., 1996).

Sensory Evaluations. Six panels of assessors of different nationalities—Spanish (A), Italian (B, D), Greek (C), British (E), and Dutch (F)—carried out the quantitative descriptive analysis (Aparicio et al., 1994b) of the 24 samples. Panels A−C strictly followed the EU regulation (EU, 1991) and the score for each attribute was the result of the overall gustatory−olfactory−tactile perception. The assessors of panels A and B were fully trained with more than five years of experience in evaluating all types of olive oil (virgin, current, lampante), and they worked at research centers. Participants of panel C were habitual consumers of this foodstuff, working at an olive oil factory. Panels D−F did not follow the EU regulation (EU, 1991) but the International Standards Organization (ISO) document "General Guidance for Establishing a Sensory Profile" (Lyon and Watson, 1994). Assessors of panel D were trained by using mixtures of different types of olive oil and were students at an Italian University. British assessors (panel E) were trained using different oils (sunflower, nut, sesame, olive, etc.), whereas the assessors of the Dutch panel F were trained by evaluating different olive oil brands. Neither the British nor the Dutch assessors had any previous experience in evaluating virgin olive oils. Table 3 summarizes the basic characteristics of the panels. Sample presentation was fully randomized, and all evaluations were done in triplicate. The assessors of each panel evaluated sensory attributes by the perceptions suggested by its panel leader. The perceptions were flavor (a combination of olfactory−gustatory−tactile and kinesthetic sensations), aroma (sensations perceived indirectly by the olfactory organ when tasting olive oil), odor (combination of sensations perceived directly through the nose), taste (sensations perceived when the gustatory papillas are stimulated), mouth feel (sensations perceived when a food comes into contact with all the sensitive areas of the mouth), and after-mouth feel/after-taste (combination of sensations perceived after the stimulus has disappeared from the mouth). Table 4 shows the sensory attributes perceived by the assessors of each panel.

The attitudes of nonhabitual consumers were studied using a panel constituted by British assessors (12 women) living most of the time in Andalusia (southern Spain) while maintaining English culinary customs.

Data Manipulation. Gas chromatographic data were linked to a personal computer, and ASCII files were manipulated by a FORTRAN program to eliminate unwanted information from the chromatographic reports. The automated program performed the selection of peaks based on retention time ranges after visual recognition of a standard chromatogram. Retention time and areas of selected peaks, including the internal standards, were stored in a database (Ultrix/SQL, 1991). Ratios of each of the selected peak areas to the area of the internal standard were used for statistical analysis. The repeatability of each chemical compound was measured using ISO 5275 (ISO-5275 1981) standard and given as relative standard deviation (% RSD_r) (coefficient of variation). The values of RSD_r were lower than 10% for all the chemical compounds excepting the following volatile compounds (Table 2), tridecene (50) 29.8%, hydrocarbon (57) 10.5% and 2-methyl-4-pentenal (60), 10.9%.

The value of each sensory attribute was calculated first from the means of the triplicate evaluations of each attribute made by the assessors of each panel and then from the mean of assessors for each attribute. This process was carried out for each panel independently.

Statistica (Statistica, 1995) was the statistical package selected. A Student−Newman−Keuls test was performed to see which products differ significantly. A Digital 486 computer was used under MS-DOS operating system.

RESULTS AND DISCUSSION

Preanalysis of Data. A study of skewness and kurtosis on each descriptor, either sensory attribute or chemical compound, showed that most of them had an almost normal distribution; hence, no transformation was applied on these. A few showed severe positive skewness, so a logarithmic transformation was applied before further analysis was performed.

All information, either chemical or sensory, was equalized by *Z* score (autoscaling) as the values of chemical compounds differ from one another (e.g., fatty acids were calculated in percentages and alcohols in milligrams per gram) and panels did not evaluate the sensory attributes by the same scale and score.

Applying the test of Student−Newman−Keuls, the four virgin olive oil varieties—Arbequina, Coratina, Koroneiki, and Picual—show significant differences at the 5% level of significance. The procedure suggested by Calvente and Aparicio (1995) was applied to select the chemical compounds and sensory attributes authenticating each variety.

Chemical Compounds and Sensory Attributes Authenticating Each Varietal Olive Oil. Figure 1 shows the standardized values (*Z* score) of the chemical compounds described in Table 1.

In Arbequina variety, concentrations of palmitic (1), palmitoleic (2), margaric (3), margaroleic (4), and linoleic (7) acids are notably high, and that of oleic acid (6) is low. The alcohols phytol (11) and octacosanol (16) appear at high concentration and docosanol (13) appears at low. However, the high concentration of sterols, campesterol (24), stigmasterol (25), and β-sitosterol (26) is noteworthy. The high concentration of phytol can be explained by the fact that this olive variety still remains green at the end of its ripening process and hence the olives contain a great amount of green pigments (Minguez-Mosquera *et al.*, 1990).

Coratina variety shows high concentrations of almost all the triterpenic alcohols—taraxerol (17), dammaradienol (18), β-amyrin (19), 24-methylene-24-dihydrolanosterol (21), and cycloarthenol (22)—and low concentrations of the aliphatic alcohols tetracosanol (14) and hexacosanol (15). The concentration of basic sterols—β-sitosterol (26) and campesterol (24)—is low but, in contrast, the concentration of methylsterols—obtusifoliol (28) and gramisterol (29)—is high.

The virgin olive oil from Picual variety can be characterized easily by its low concentration of sterol Δ_5-avenasterol (27), but mainly by the low concentration of some aliphatic and triterpenic alcohols—taraxerol

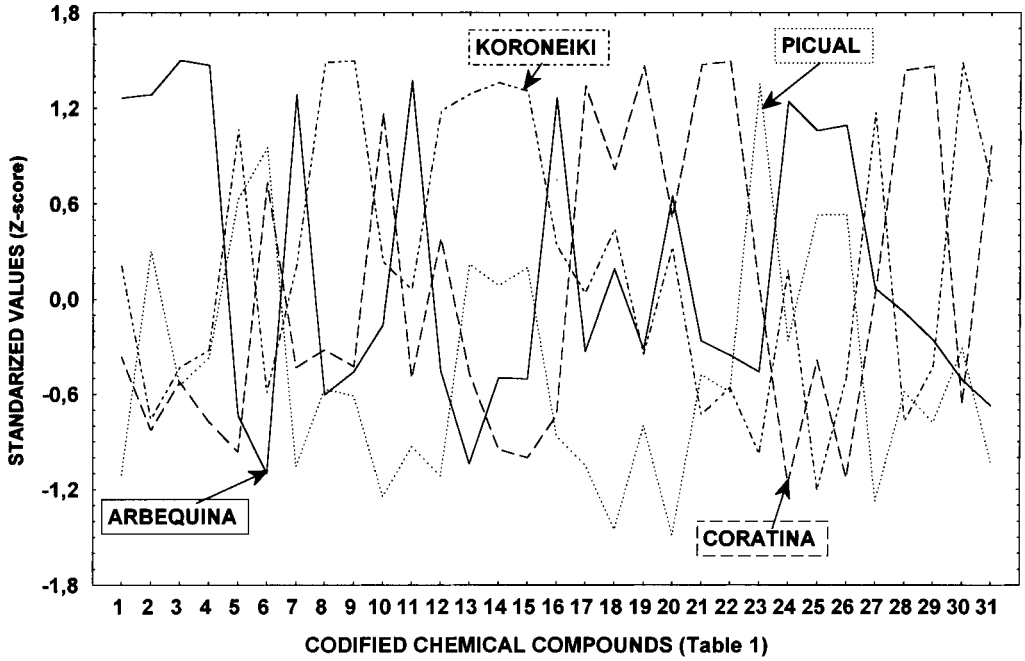

Figure 1. Concentration of nonvolatile compounds: fatty acids, alcohols, sterols, and methylsterols. The concentrations have been autoscaled (*Z* score) in order to see them in a similar range. Codes are described in Table 1.

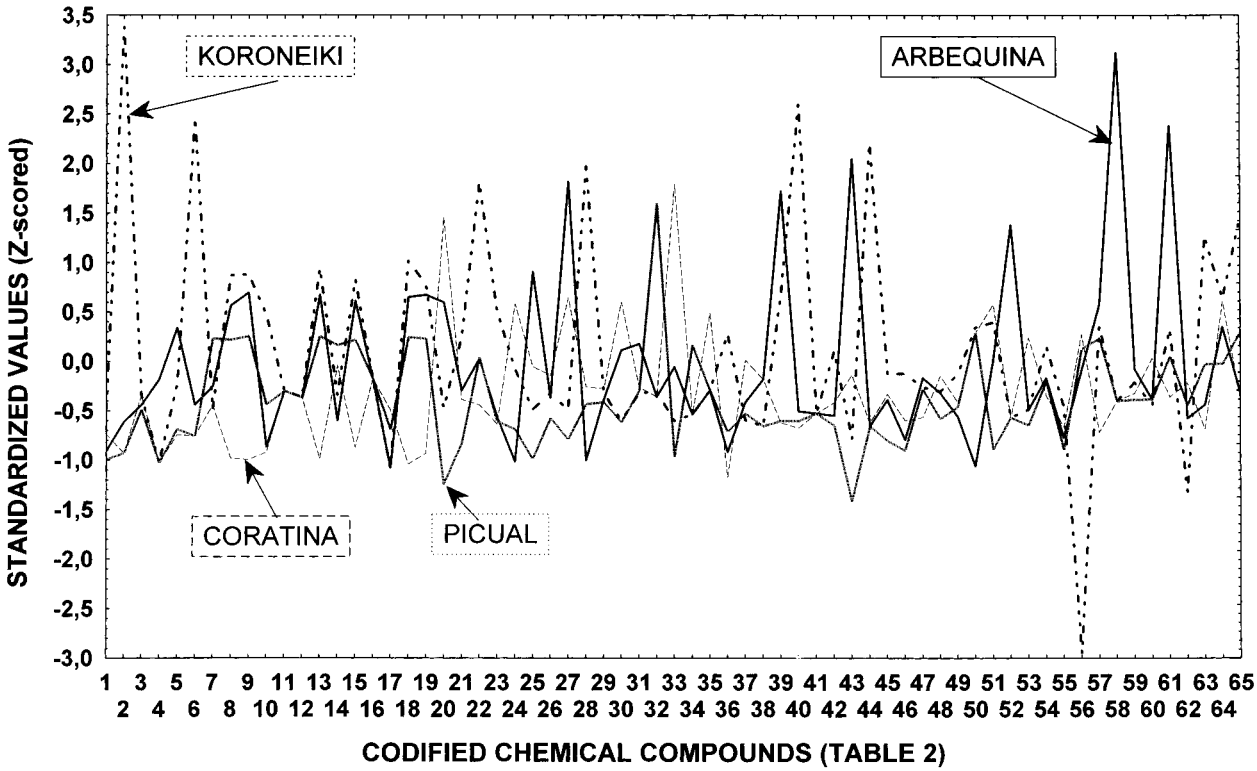

Figure 2. Concentration of volatile compounds: esters, aldehydes, alcohols, ketones, hydrocarbons, furans, and acids. Concentrations have been autoscaled (*Z* score) in order to see them in a similar range. Codes are described in Table 2.

(17), β-amyrin (19), butyrospermol (20), phytol (11), and erythrodiol (12)—and a high concentration of 24-methylenecycloarthanol (23). The low concentration of linoleic acid (7) is remarkable since it is one of the precursors of volatile compounds responsible for the variety's sensory characteristics.

The variety Koroneiki shows high concentration of cycloeucalenol (30) methylsterol, erythrodiol (12) alcohol, and almost all aliphatic alcohols—docosanol (13), tetracosanol (14), and hexacosanol (15). However, the high concentration of linolenic (8) acid, together with arachidic (9) acid, is the most remarkable characteristic of this virgin olive oil variety as the former is the precursor of some volatile compounds.

The volatile compounds (Figure 2) responsible for aroma were characterized by sniffing. Since the information of sniffing is in fact a free choice of sensory attributes by assessors (Morales *et al.*, 1994), the attributes were standardized in seven groups of sensory attributes: bitter—pungent—astringent, undesirable, ripe fruit, fruity, sweet, fruity olives, and green, using the statistical sensory wheel (Aparicio *et al.*, 1996).

Arbequina variety is clearly characterized by the low concentration of (*Z*)-3-hexenal (28) and high concentra-

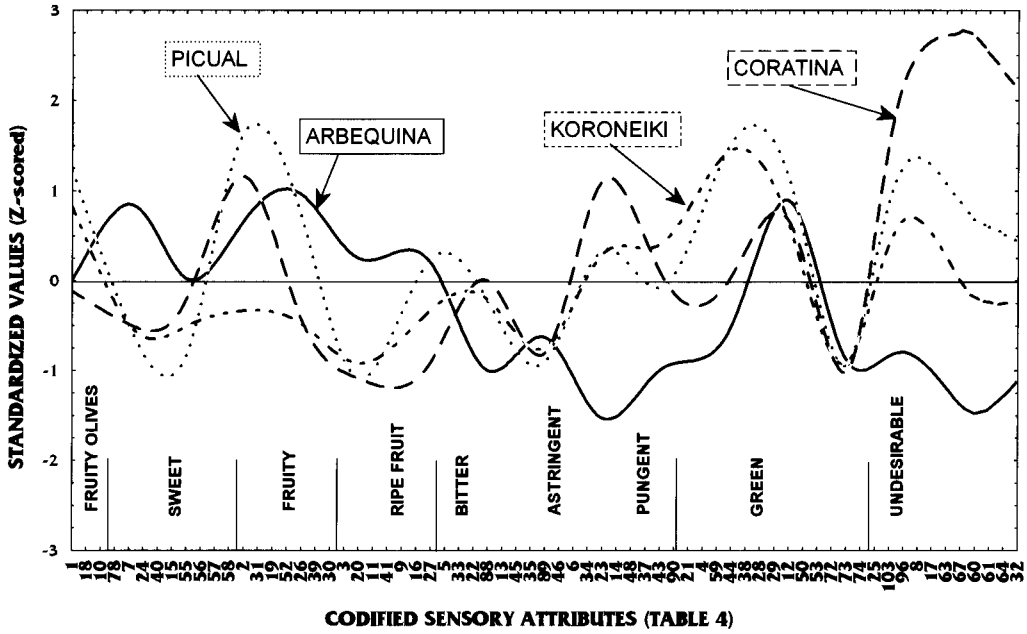

Figure 3. Sensory profiles of the sensory attributes evaluated by panels. The profiles have been built by a polynomial spline. Codes are described in Table 4.

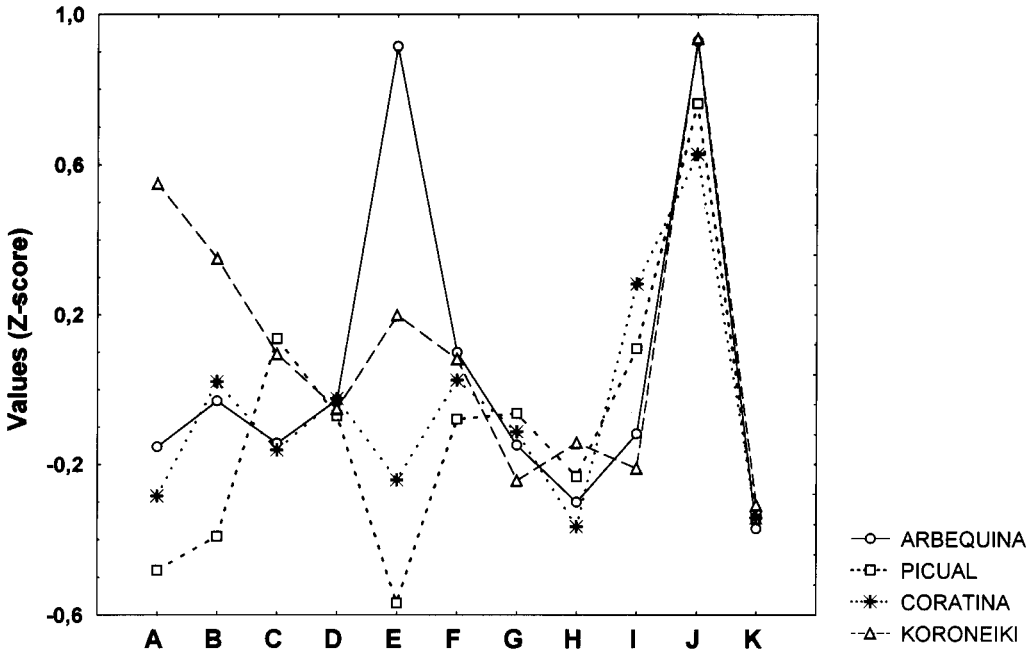

Figure 4. Total concentrations of the volatile chemical compounds: esters (A), hydrocarbons (B), ketones (C), alcohols (D), furans (E), aldehydes (F), and acids (G). Total concentrations of the nonvolatile compounds: aliphatic alcohols (H), triterpenic alcohols (I), sterols (J), and methylsterols (K).

tion of (*E*)-3-hexenal (27), ethenylbenzene (39), 4-methyl-1-penten-3-ol (58), and a C_6-branched (61) alcohol. The high concentration of linoleic acid (7) explains the high concentration of hexanal (19) as the latter is produced from the former, its precursor, through the lipoxygenase pathway (Vick and Zimmerman, 1987). On the other hand, the sensory attributes of these compounds (fourth column of Table 2) show that Arbequina has low levels of astringency and bitterness and a high level of ripe fruity aroma. This sensory profile seems in disagreement with the green color (typical of unripe fruits) of this variety, which remains green during the whole ripening process. The great amount of pigments in the olive epicarp of this variety is produced by a biochemical pathway (Minguez *et al.*, 1990) alternate to those by which the volatile compounds are produced (Vick and Zimmerman, 1987).

Picual variety is characterized by the high concentration of (*Z*)-2-hexenal (32) and the low concentrations of (*E*)-3-hexenal (27) and 3-(4-methyl-3-pentenyl)furan (43) (as opposed to the case of Arbequina), a hydrocarbon (20), (*Z*)-2-pentenal (25), (*E*)-2-hexenal (33), and (*Z*)-3-hexen-1-ol (51). This variety of olive oil has no clear sensory characterization from the volatile compounds, although its profile shows the oil is bitter with neither sweet aromatic nor ripe fruit attributes. A possible explanation for this sensory profile can be found in the low concentration of linoleic acid, which is responsible

for the low concentrations of hexanal (19) and hexyl acetate (40), volatile compounds that are responsible for sweet and green perceptions.

Virgin olive oils of Koroneiki variety have high concentrations of octene (2),1,3-hexadien-5-yne (6), 2-methyl-1-propanol (22), (*Z*)-3-hexenal (28), hexyl acetate (40), 3-hexenyl acetate (44), 2-octenal (63), and a hydrocarbon (65), but low concentrations of a C_{11} hydrocarbon (56) and (*Z*)-2-hexen-1-ol (62). The high concentration of linolenic acid can explain the high concentration of (*Z*)-3-hexenal (28) that is produced, within the lipoxygenase pathway, from the 13-hydroperoxide of this fatty acid by the action of the enzyme hydroperoxide lyase (Vick and Zimmerman, 1987). With regard to the sensory profile, all these volatiles are exclusively characterized by the green (banana, fruity) sensory attribute and neither bitter nor pungent sensory attributes qualify the olive oils of Koroneiki variety.

The virgin olive oils obtained from Coratina variety are characterized by the high concentrations of a hydrocarbon (20), (*E*)-2-hexenal (33) (both in contrast to the case of Picual), an alcohol (24), 3-methylbutyl acetate (30), and 3-methyl butanol (35) and low concentrations of ethylfuran (8), ethyl propanoate (9), pent-1-en-3-one (13), a hydrocarbon (15), butyl acetate (18), and hexanal (19). The sensory attributes, which basically qualify the volatile compounds, have enabled this variety of oil to be characterized as bitter, low sweet-fruity, either strawberry or apple, and a little undesirable.

From the data set of sensory attributes evaluated by panels (Table 4), 67 sensory attributes were selected for their contribution to the sensory evaluation of virgin olive oil (Aparicio *et al*., 1994b, 1996; Aparicio and Morales, 1995; Morales *et al*., 1995) and because the nonselected attributes are strongly correlated ($R \geq 0.95$) with those selected. As there are sensory attributes with the same semantic term, or attributes with different semantic terms but equal sensory perception, it is not easy to show obvious contributions of the sensory attributes to the characterization of olive oil varieties. In order to minimize this drawback, the selected sensory attributes have been clustered into groups suggested by the statistical sensory wheel. Figure 3 shows the sensory profiles of these oils using a mathematical procedure (fit, spline; order of polynomial, 10^5; base of logarithm, decimal; stiffness, 0.37; fit line quality, perfect). The information from the sensory profiles has been summarized in the following points: Arbequina, high values of attribute fruity (tomato and apple sensory attributes) and low values of bitter, pungent and astringent; Koroneiki, green and slightly astringent; Picual, high values of attributes fruity (tomato and artichoke) and pungent and slightly undesirable; Coratina, high values of all sensory attributes clustered inside the attribute undesirable and those inside the attributes bitter and pungent. Other sensory attributes are sweet (odor) and green olives.

A study carried out by McEwan (1994) showed that the high values of some attributes, such as astringent, are determinant for rejection of a virgin olive oil by British consumers, as such oils are qualified with the lowest values of overall acceptability. The conclusions suggested by McEwan (1994) have allowed a regression equation to be designed that has been applied to calculate the overall acceptability of nonhabitual consumers; structured scale, score 1−10. According to the results of the formula, the virgin olive oil varieties were classified in the following ranges: Arbequina, 7.07−8.24; Coratina, 3.45−6.46; Koroneiki, 6.30−7.29; Picual, 4.91−7.33.

The information of the overall acceptability by British consumers was checked with other British assessors who qualified the oils in terms of sensory phrases that represent what the assessors think of them. Since there are different types of virgin olive oil, depending on the extraction systems used—centrifugation, percolation and pressing—and the stages of olive maturity—underripe, normal ripe, and overripe—there are contradictory phrases; nevertheless, the phrases do show the assessors' feelings about the varietal virgin olive oils. The following phrases are the most remarkable ones suggested by assessors: Arbequina, slightly lighter in taste and scented, slightly sweet and palatable, mild olive flavor, pleasant, no bitter aftertaste, no harshness, mellow vegetable taste, quite fruity, fresher taste, etc.; Coratina, tastes like grass, a little harsh, unpleasant bitter taste, a bit fatty, yuk, sweetly perfumed, etc.; Koroneiki, smells green and fresh, smells strong, pleasant fresh smell, pleasant odor, oily green smell, nice sweet, etc.; Picual, fruity smell, pungent smell, slightly lemon, smell of olives, strong smell but not quite so offensive, fresh smell, etc.

CONCLUSIONS

Figure 4 summarizes the basic chemical characteristics of these virgin olive oil varieties. From this figure it can be inferred that there are inherent characteristics to these varieties. However, knowing the olive oil biochemical pathways is not enough to give plausible explanations of why the varieties have higher or lower concentrations of some series of chemical compounds. Wherever it was possible, e.g., hydroperoxides of fatty acids, the concentrations of certain chemical compounds have been explained.

From an exclusively chemical point of view, esters and furans (volatile compounds) and alcohols, both aliphatic and triterpenic, can easily characterize the varieties. The variety Koroneiki shows the maximum concentration of esters, responsible for the green (grass) perception, while Arbequina has the maximum concentration of furans, which are responsible for sweet (ripe fruit) perception. These sensory characterizations from the volatile compounds agree with the sensory evaluation carried out by the assessors. The total concentration of furans is able to distinguish Picual and Koroneiki varieties from Coratina and Arbequina—the former varieties are picked when they are completely black while the latter varieties are still green when harvested.

Alcohols, basically triterpenic, can authenticate the varieties, while methylsterols and the volatile alcohols, acids, and, perhaps, aldehydes do not show substantial differences between varieties.

Finally, the sensory authentication of the olive oil varieties by the sensory panels has been cross-validated with the volatile compounds and their sniffing, so opening a way for a basic sensory authentication of olive oil varieties by their volatile chemical compounds.

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