Relationships between volatile compounds and sensory characteristics in virgin olive oil by analytical and chemometric approaches

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Abstract

BACKGROUND: The volatile fraction of virgin olive oil is characterised by low molecular weight compounds that vaporise at room temperature. In order to obtain an aroma profile similar to natural olfactory perception, the composition of the volatile compounds was determined by applying dynamic headspace gas chromatography, performed at room temperature, with a cryogenic trap directly connected to a gas chromatograph–mass spectrometer system. Samples were also evaluated according to European Union and International Olive Council official methods for sensory evaluation. In this paper, the composition of the volatile fraction of 25 extra virgin olive oils from different regions of Italy was analysed and some preliminary considerations on relationships between chemical composition of volatile fraction and sensory characteristics are reported.

RESULTS: Forty-two compounds were identified by means of the particular analytical technique used. All the analysed samples, classified as extra virgin by the panel test, never present peaks whose magnitude is important enough in defected oils. The study was focused on the evaluation of volatile compounds responsible for the positive impact on olive odour properties ('green–fruity' and 'sweet') and olfactory perception.

CONCLUSION: Chemometric evaluation of data, obtained through headspace analysis and the panel test evaluation, showed a correlation between chemical compounds and sensory properties. On the basis of the results, the positive attributes of virgin olive oil are divided into two separated groups: sweet types or green types. Sixteen volatile compounds with known positive impact on odour properties were extracted and identified. In particular, eight compounds seem correlated with sweet properties whereas the green sensation appears to be correlated with eight other different substances. The content of the compounds at six carbon atoms proves to be very important in defining positive attributes of extra virgin olive oils and sensory evaluation.

Keywords: dynamic headspace analysis; gas chromatography–mass spectrometry; virgin olive oils; sensory evaluation; chemometric evaluation

INTRODUCTION

The volatile fraction of virgin olive oil has been the subject of numerous investigations carried out by several researchers over a number of years.[1–10] The principal aim of these studies was to obtain flavour profiles that could be correlated with the sensory characteristics of the samples: in this way, positive attributes and sensory defects in olive oil could be associated with chemical compounds present in the volatile fraction. As is well known, olive oil quality is based upon consumer perceptions of aroma, and the absence of sensory defects is necessary for the oil to be classified as 'extra virgin'. For this reason, virgin olive oils were the first foods requiring sensory evaluation as part of their legal control. Quality olive oil assessment involves evaluation of sensory characteristics, which was carried out according to the 'panel test' method, a standardised sensory method that classifies oils on the basis of the presence or absence of standardised defects and of the presence of positive characteristics named 'fruity', 'bitter' and ' pungent'. The panel test was introduced in the 1990s in accordance with Commission Regulation (EEC) 2568/91[11] and an International Olive Oil Council (IOOC) trade norm;[12] later, a modified version was developed by the IOOC[12,13] and adopted by the European Economic Community (EEC).[14]

To obtain flavour profiles, a number of different analytical approaches were explored, but the analytical chemistry applied to food composition studies was oriented to the reduction of sample manipulation with the aim of reducing the formation of analytical artefacts and use of solvents.

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Headspace techniques are the most suitable ones for the study of aroma compounds, and among the different methods used to sample the volatile components of the headspace, dynamic sampling has been shown to be the most suitable as it does not introduce discrimination in the volatile components analysed.[15,16] These methods have several advantages, such as being quicker, simpler and highly reproducible. Moreover, if they are used at room temperature and without adsorbent material, they yield an aroma profile that closely resembles natural olfactory perception, as there is little chance of artefact formation. A particular dynamic headspace gas chromatography (DHS-GC) solvent-free device developed by Barcarolo and Casson[17] incorporated a reverse-flow step in order to avoid any contamination of the analytical gas chromatography column with gases or other substances that could not be condensed.

In a previous paper,[18] we carried out the characterisation of defective oils by headspace analyses of a number of oil samples that were also characterised by a panel, in order to determine whether a relationship exists between compounds (off-flavours) in the headspace and sensory evaluation. In another study,[19] we analysed the volatile fraction of the most representative commercial truffle-flavoured oils: the headspace technique allows the evaluation of the complexity of flavour determined by the use of real truffles rather than synthetic aromas.

In this paper, we have applied headspace analysis to a number of oil samples that were also characterised by a panel as 'extra virgin' olive oils. The aim of this study was to highlight a relationship between low molecular weight compounds in the headspace, which vaporise at room temperature, and sensory evaluation. For this reason, purge-and-trap sampling performed at room temperature was applied. The objectives of the present study highlight a correlation between the sensory impact of compounds in *regio olfattoria* with the chemical composition of the volatile fraction of the samples analysed and explore the possibility of obtaining a classification of samples by chemometric evaluation of the volatiles pattern.

MATERIALS AND METHODS

Sampling

Twenty-five samples of virgin olive oils obtained from different olive cultivars (Leccino, Arbequina, Gentile, Buga, Bianchera, Pendolino, Dritta, Itrana, Tondo Iblea, Tortiglione, Coratina, Raggia, Intosso, Toccolana and Nocellara) were analysed. The samples were collected directly at the mill by using dark bottles (500 mL) fully filled (two bottles for each sample); one sample was rapidly sent for sensory analysis, while the other one was rapidly sent to the chemistry laboratory with a fast delivery agency. Bottles were sent in a refrigerated box to avoid any heat problems. Once the samples had reached the laboratories, they were stored at 15 °C until analysed.

Sensory analysis

Each sample was evaluated by a panel, according to the official method used within the framework of Commission Regulation (EEC) 2568/91[11] modified by Regulation EC 796/02.[14] The panel comprised nine tasters, each trained in compliance with EEC Regulation 2568/91 along with 9 years' experience in the sector. The panel works within the framework of Italian public administration. The applied protocol was as cited above: every sensory evaluation session assessed three samples, with mouth cleaning by mean of green apple slices, while the order of presentation of samples to assessors was established by the head of panel after a preliminary assessment.

On the basis of the data obtained for the analysed sample, the totality of the oils were classified as extra virgin and so it has been possible to determine the principal positive olive oil odour properties (fruity, green, bitter, pungent and sweet).

Headspace sampling and analysis

Analysis of volatile compounds was carried out by means of the analytical system developed by Barcarolo and Casson.[17] The oil sample (about 7.0 ± 0.1 g) was weighed exactly into a 10 mL vial, then 0.02 μL (13.8 μg) of isooctane (J.T. Baker, Deventer, Netherlands) was added as internal standard and the vial was immediately sealed with an aluminium rubber septum (Supelco Inc., Bellefonte, PA, USA) and conditioned at 35 °C for 15 min before the analysis. The sample was purged by bubbling with helium: the stripping was carried out for 150 s with helium at a rate of 10 mL min^{-1}. Volatile components were driven into a capillary tube that was inside a cryogenic trap (liquid nitrogen) maintained at −110 °C, and connected in an on-column mode to a capillary gas chromatograph (Carlo Erba GC 8000; Carlo Erba, Milan, Italy). The cryogenic trap, which was represented by a fused silica capillary tube, did not show activated adsorbent or porous polymers. This trap allows the acquisition of an aroma profile similar to natural olfactory perception without artefacts or problems related to saturation, competition between volatiles and incomplete or irreversible adsorption. At the end of sampling (purging) time, desorption of volatile components takes place by heating the trap to 240 °C in 5 s and then by transferring volatiles to the capillary column in 15 s. The analytical column used was a capillary fused-silica column 50 m × 0.32 mm I.D., coated with PS 264 (Mega, Milan, Italy) and of 3 μm film thickness. The capillary gas chromatography system was coupled directly to a MD 800 mass spectrometer (Carlo Erba). Gas chromatographic conditions were the following: oven initial temperature 40 °C, held for 6 min, then programmed to 180 °C at a rate of 5 °C min^{-1}, then 5 min at 180 °C, then at 7 °C min^{-1} to 200 °C, held for 3 min, and finally at 10 °C min^{-1} to 220 °C with 5 min of final isotherm. The transfer line temperature was kept at 250 °C.

The mass spectrometer scanned from m/z 29 to m/z 300 at 0.5 s cycle time. The ion source was set at 180 °C and spectra were obtained by electron impact (70 eV).

The tentative identification of compounds was carried out through a study of the MS spectra and comparison with members of the NBS library.

Quantitative evaluation was carried out by using the internal standard method: we set the response factor as unity for each substance, so it was possible to give quantitative data as internal standard equivalents and to compare the content of each component in the analysed samples.

Statistical analysis

The sensory and analytical data were first separately analysed applying principal component analysis to assess the internal degree of correlation of the variables in the two groups. Biplot was used to describe the correlation structure of the variables and the scores of the observations on the two components.

The relationship among the variables of the two groups was investigated using partial least squares (PLS) regression. Sensory descriptors were considered as dependent variables (matrix Y), analytical data as covariates (matrix X) in the multivariate linear regression model $Y = X\beta$, where β is the matrix of coefficients.

PLS builds a sub-set of predictors from *X* and a sub-set of response variables from *Y* so that the correlation between the two new sets of variables is maximised. Variables were centred and scaled to eliminate the effect of different measurement units. Cross-validated root mean square error of prediction was used to determine the number of components. The analysis was conducted by using R ver 3.0.1[20] and Statistic-a ver. 10 (StatSoft Inc., Tulsa, OK, USA).

RESULTS AND DISCUSSION

Forty-two volatile components were extracted and identified by using a particular preliminary analytical technique (Table 1). The volatile substances could be grouped according to chemical classes: alcohols, aldehydes, esters, ketones, sulfur compounds and terpenes.

Twelve alcohols were identified. Our sampling technique allowed the detection of low molecular weight compounds, such as methanol, which could originate from pectin hydrolysis, and ethanol, which could be related to glucose fermentation. The concentration of methanol ranged between 880 and 4300 $\mu g\ kg^{-1}$, while the ethanol concentration ranged between 776 and 7160 $\mu g\ kg^{-1}$. The amount of five alcohols that are associated with the amino acids catabolism is very low and homogeneous. In particular, the concentration of 2-butanol and 2-methyl-3-buten-2-ol ranged between 0 and 10 $\mu g\ kg^{-1}$, while the content of isobutanol ranged between 11 and 172 $\mu g\ kg^{-1}$, and the concentration of 3-methyl-1-butanol and 2-methyl-1-butanol ranged between 7 and 360 $\mu g\ kg^{-1}$. The formation of these compounds is correlated with the catabolism of valine and leucine, which are converted to volatile compounds, including methyl-branched alcohols.[21] Generally, the high content of these compounds presents a negative impact on olive oil odour properties and could be related, according to the results of the panel test, to the muddy and fusty defects.[18] In addition, C5 and C6 alcohols were identified. The C5 alcohols identified were 1-penten-3-ol, in a range between 91 and 511 $\mu g\ kg^{-1}$, and 1-pentanol and 2-pentenol, in a range between 0.6 and 104 $\mu g\ kg^{-1}$. 3-Hexenol and 2-hexenol were the two major C6 alcohols identified. As is well known, these compounds are derived from the lipoxygenase pathway that involves a series of enzymes that oxidise, cleave (hydroperoxide lyase) and are reduced to alcohols (alcohol deydrogenase).[22] The major concentration of 2-hexenol, in a range between 40 and 606 $\mu g\ kg^{-1}$, compared to 3-hexenol, supports higher lipoxygenase activity for linolenic acid than linoleic acid and the instability of 3-hexenal that rapidly isomerises to a more stable compound, 2-hexenal: the aldehydes formed are further reduced to alcohols by alcohol deydrogenase activity.

In the analysed samples, 15 aldehydes were identified. Chain length is correlated with the origin of compounds and influences flavour perception: in particular, compounds with low carbon number are generally associated with malty fruit that is correlated with improper fruit handling and possible origin of sensory defects, C5 and C6 aldehydes having positive impact on olive oil odour properties[23] while long chain aldehydes, with seven to 10 carbon atoms, characterise the sensory defect associated with oxidation reactions.[24,25] Acetaldehyde, 2-propenal, propanal, 2-butenal and butanal may be correlated with sensory defects.[18] The content of these aldehydes in the analysed samples was very low, in compliance with good olive oil quality. The concentration of methyl-branched aldehydes, isobutanal, in a range between 14 and 360 $\mu g\ kg^{-1}$, 3-methylbutanal and 2-methylbutanal, in a range between 28 and 703 $\mu g\ kg^{-1}$, generally associated with conversion of leucine and valine, was relatively high. It may be interesting to observe that the content of these compounds in International Olive Oil Council (IOOC) standard defective oils[18] was very low. C5 (pentanal) and C6 (hexanal, 2-hexenal and 3-hexenal) aldehydes are the most abundant compounds in the volatile fraction of virgin olive oils: the contribution of these components is crucial to olive oil quality and is related to the positive attributes of flavour. The content of long-chain aldehydes identified in the samples was low and homogeneous. In particular, the concentration of 2-heptenal ranged between 0.6 and 5.52 $\mu g\ kg^{-1}$, octanal ranged between 0.84 and 24 $\mu g\ kg^{-1}$ and nonanal ranged between 3.7 and 25.8 $\mu g\ kg^{-1}$. These compounds can be considered as markers of oxidation and the very low content showed a good quality of the analysed samples.

Three esters were identified: the presence of these compounds could be related to the content of the methyl and ethyl alcohol in the samples and fatty acid metabolism. The concentration of methylformate was very low, in a range between 0 and 33 $\mu g\ kg^{-1}$, while the content of methylacetate was greater, in a range between 11 and 389 $\mu g\ kg^{-1}$, and ethylacetate, in a range between 18 and 470 $\mu g\ kg^{-1}$. These esters are important constituents of many fruits and are generally linked to the positive fruity aroma of olive oil. Generally, the formation of volatile esters involves the alcohol acetyl transferase action, but the activity towards short chain alcohols appears very low: this suggests that ethyl acetate may be synthesised through a different pathway.[26]

Ketones are an important group of volatile compounds identified in the virgin olive oils. Our sampling technique allowed the detection of seven compounds. The presence of ketones in the aroma profile of virgin olive oil is probably related to the activity of indigenous microflora in the fruit. Acetone was the smaller ketone identified in the aroma profile: the concentration of the compound, in a range between 55 and 1008 $\mu g\ kg^{-1}$, could have an important impact on olive oil odour properties. The concentration of C4 compounds identified, 2-butenone and 2-butanone was low, generally less than 100 $\mu g\ kg^{-1}$, while the most abundant ketones identified were C5 ketones, 2-pentanone and 3-pentanone. The concentration of these compounds ranged between 50 and 706 $\mu g\ kg^{-1}$ and between 7 and 365 $\mu g\ kg^{-1}$, respectively. C5 ketones are generally linked to positive sensory characteristics and these compounds were proposed as markers of virgin olive oil quality.[27] Two more ketones, 2-hexanone and 2-heptanone, were identified in the aroma profile of samples analysed: the concentration of these compounds was very low, minor to 4 $\mu g\ kg^{-1}$.

Additionally, in the volatile fraction of samples, two sulfur compounds were identified. The concentration of methylthiomethane, in a range between 0 and 73 $\mu g\ kg^{-1}$, appears variable in individual samples, while the content of dimethylsulfone, in a range between 0 and 5 $\mu g\ kg^{-1}$, was low and homogeneous. These minor volatile compounds, mainly formed from methionine, cysteine and cystine via Strecker degradation,[28] have received poor attention with regard to their presence in the volatile olive oil fraction, but on the basis of their very low perception threshold, these compounds could give an important contribution to the aroma profile of virgin olive oil.

Data obtained from GC-MS analysis as well as through the panel test were treated using chemometric methods. The principal component analysis applied on the sensory data (Fig. 1) gave very good results: the first two components account for 90% of total variation

Table 1. Volatile compounds (μg kg^{-1}) in the examined samples of virgin olive oil

Rt (min)	Compound	Gentile 1	Gentile 2	Gentile 3	Leccino 4	Leccino 5	Leccino 6	Leccino 7	Leccino 8	Intosso 9	Buga 10	Bianchera 11	Pendolino 12	Dritta 13
4.20	Acetaldehyde	99.4 ± 10.9	14.95 ± 1.3	108 ± 13	162 ± 16	72.5 ± 7.4	134 ± 12	72.4 ± 5.8	107 ± 12	128.4 ± 15	4.75 ± 0.43	21.1 ± 2.1	57.9 ± 6.95	36.6 ± 3.6
4.28	Methanol	4101 ± 398	2433 ± 254	3133 ± 297	3914 ± 401	1618 ± 168	314 ± 37	3222 ± 354	4328 ± 414	3015 ± 287	1541 ± 145	1473 ± 153	2612 ± 279	1678 ± 189
5.05	Methylformate	ND	ND	22.23 ± 2.7	18.63 ± 1.9	24.7 ± 3.2	18.32 ± 2.1	28 ± 3.4	ND	33.9 ± 3.8	ND	ND	ND	24.1 ± 2.9
5.91	Ethanol	7161 ± 502	4359 ± 349	4364 ± 350	4171 ± 255	3644 ± 240	4404 ± 330	5089 ± 407	6606 ± 462	6379 ± 511	1387 ± 85	1226 ± 66	4324 ± 346	2468 ± 222
6.87	2-Propenal	33.7 ± 1.4	10.81 ± 0.4	45.5 ± 2.1	7.07 ± 0.3	22.5 ± 1.81	11.55 ± 0.5	6.66 ± 0.23	19.4 ± 1.2	34.5 ± 2.2	4.01 ± 0.14	8.28 ± 0.38	12.1 ± 0.68	22.4 ± 1.7
7.08	Acetone	223.1 ± 24	178.2 ± 18	196 ± 20	378 ± 42	325 ± 34	192.8 ± 21	80.8 ± 7.84	65.3 ± 5.5	731 ± 95	157.8 ± 14	133.1 ± 10	140 ± 12.5	576 ± 63.5
7.67	Propanal	35.8 ± 2.5	9.62 ± 0.5	38.93 ± 2.3	31.3 ± 1.7	27.9 ± 1.9	25.06 ± 1.8	30.4 ± 2.41	25.1 ± 1.7	29.3 ± 2.3	27.9 ± 2.2	16.92 ± 0.9	35 ± 2.11	19.9 ± 1.78
8.47	Methylthiomethane	ND	ND	10.9 ± 0.5	ND	4.39 ± 0.26	6.94 ± 0.35	27.1 ± 1.65	58.3 ± 4.1	ND	9.03 ± 0.45	16.35 ± 1.0	28.2 ± 1.67	ND
8.81	Methylacetate	76.9 ± 3.1	97.8 ± 4.9	110.6 ± 6.1	135 ± 6.7	174.5 ± 8.7	171.2 ± 18	228.2 ± 14	307 ± 25	389 ± 20	37.3 ± 2.1	132.5 ± 10.6	181 ± 12.7	157 ± 7.9
9.33	Dimethylsulfone	2.35 ± 0.2	2.21 ± 0.2	ND	ND	ND	5.39 ± 0.43	ND	ND	1.92 ± 0.13	ND	ND	1.29 ± 0.08	ND
10.13	Isobutanal	216.3 ± 26	263 ± 24	360 ± 38	123.4 ± 12	107.4 ± 12	171.5 ± 19	187 ± 18	232.5 ± 25	195 ± 19	43.4 ± 3.9	126 ± 11.7	110.6 ± 9.8	136.7 ± 15
10.61	2-Butenal (crotonal)	7.37 ± 0.5	4.86 ± 0.4	7.24 ± 0.7	15.36 ± 1.1	23.42 ± 1.6	19.72 ± 1.6	9.21 ± 0.65	3.42 ± 0.18	29.8 ± 2.45	30.3 ± 2.4	11.4 ± 0.74	9.95 ± 0.65	23.41 ± 1.9
11.75	2-Butenone	2.88 ± 0.3	2.51 ± 0.3	1.82 ± 0.18	2.48 ± 0.2	1.6 ± 0.21	3.25 ± 0.3	6.96 ± 0.84	1.07 ± 0.09	5.17 ± 0.72	1.2 ± 0.13	1.84 ± 0.24	0.93 ± 0.11	1.55 ± 0.23
11.87	Butanal	2.84 ± 0.4	2.57 ± 0.4	3.72 ± 0.4	2.56 ± 0.3	2.82 ± 0.4	1.6 ± 0.14	3.43 ± 0.3	2.31 ± 0.27	7.4 ± 1.15	2.07 ± 0.18	3.96 ± 0.51	2.24 ± 0.25	7.81 ± 1.25
12.22	2-Butanone	19.8 ± 1.9	15.31 ± 1.4	21.2 ± 2.2	102.2 ± 11	34.25 ± 3.5	62.16 ± 5.9	42.1 ± 3.9	27.1 ± 2.8	109 ± 9.7	30.8 ± 4.1	27.1 ± 2.9	25.9 ± 2.25	76.5 ± 7.9
12.54	2-Butanol	ND	0.9 ± 0.06	1.8 ± 0.2	ND	ND	0.59 ± 0.07	1.2 ± 0.13	0.88 ± 0.11	2.81 ± 0.34	1.15 ± 0.17	0.82 ± 0.07	ND	1.51 ± 0.19
12.91	2-Methyl-3-buten-2-ol	3.35 ± 0.4	3.51 ± 0.5	3.16 ± 0.4	3.81 ± 0.5	1.5 ± 0.18	4.88 ± 0.58	3.67 ± 0.37	1.86 ± 0.29	4.7 ± 0.61	1.55 ± 0.23	1.48 ± 0.16	2.15 ± 0.32	ND
13.07	Ethylacetate	208.7 ± 27	213 ± 25	150 ± 14.7	312.2 ± 29	315 ± 33	111 ± 10.9	176.2 + 18	165.7 ± 16	473 ± 52	84.8 ± 8.8	60.5 ± 8.4	398 ± 56	380 ± 42.3
13.77	Isobutanol	109.9 ± 14	74.6 ± 7.9	75.7 ± 8.1	99.15 ± 15	24.5 ± 2.7	103.6 ± 12	104.5 ± 10	149 ± 18	173 ± 26	11.3 ± 1.21	12.04 ± 1.35	44.6 ± 5.8	84.1 ± 8.9
15.27	3-Methylbutanal	494 ± 51	473 ± 50	652 ± 85	120 ± 12	195 ± 20	183.3 ± 17	484 ± 53	438 ± 47	144.3 ± 13	117.1 ± 9.9	203 ± 24.3	211 ± 22.9	246 ± 26.1
15.81	2-Methylbutanal	704 ± 72	561 ± 60	716 ± 67	120 ± 11.7	199 ± 21.5	226 ± 18.4	413 ± 41	391 ± 40	214 ± 19	140.1 ± 13	243 ± 26	203.4 ± 22.6	232 ± 22.8
16.69	1-Penten-3-ol	360 ± 35	244.3 + 25	347 ± 37	323 ± 32	108.7 ± 9.2	369 ± 35	338 ± 35	280 ± 26.5	251 ± 22.7	245 ± 26.5	287 ± 29.4	359 ± 38.3	91.5 ± 8.4
16.93	2-Pentanone	399 ± 52	396 ± 42	417 ± 46	435 ± 45	312 ± 29	492 ± 70	489 ± 75	539 ± 69	50.1 ± 5.8	393 ± 42	385 ± 39.5	457 ± 66.5	221 ± 21.5
17.15	Isooctane (i.s.)	–	–	–	–	–	–	–	–	–	–	–	–	
17.49	Pentanal	448 ± 48	383.3 ± 41	381 ± 37	443 ± 53	490 ± 55	472 ± 64	537 ± 73	670 ± 73	560 ± 59	251 ± 24.6	489 ± 63	501 ± 59	387 ± 46.4
17.67	3-Pentanone	19.81 ± 1.9	15.37 ± 1.6	17.2 ± 1.8	57 ± 4.9	138 ± 14.8	65.6 ± 7.2	55.6 ± 5.8	20.8 ± 2.22	360 ± 38	366 ± 44	299 ± 29	181 ± 17.5	115 ± 13.2
19.38	3-Methyl-1-butanol	97.3 ± 6.9	46.3 ± 4.5	65.4 ± 5.2	95.5 ± 8.8	31.6 ± 2.5	65 ± 6.2	81.2 ± 7.6	129.4 ± 11	172.4 ± 15	39.5 ± 3.5	34.6 ± 2.42	51.7 ± 4.78	92.5 ± 8.8
19.61	2-Methyl-1-butanol	71.9 ± 7.6	36.22 ± 4.1	47 ± 4.9	59.1 ± 7.1	20.04 ± 2.6	57.5 ± 6.2	81.5 ± 8.6	68.8 ± 7.2	103.5 ± 12	14.6 ± 1.51	16.08 ± 1.8	30 ± 3.3	25 ± 2.84
21.02	1-Pentanol	3.98 ± 0.3	1.38 ± 0.12	2.14 ± 0.2	3.17 ± 0.3	2.18 ± 0.18	18.02 ± 2.4	10.54 ± 1.1	6.74 ± 0.6	9.63 ± 0.78	8.37 ± 0.67	10.1 ± 1.21	15.6 ± 2.24	0.63 ± 0.04
21.22	2-Pentenol	85.23 ± 6.9	29.51 ± 2.9	56.4 ± 5.8	58.32 ± 6.1	10.7 ± 0.9	84 ± 6.7	65.2 ± 6.3	38.5 ± 3.9	36.5 ± 3.6	50.4 ± 4.9	66.4 ± 6.23	77.2 ± 7.1	9.78 ± 0.87
22.24	2-Hexanone	ND	ND	ND	1.01 ± 0.13	ND	ND	ND	1.28 ± 0.15	1.3 ± 0.17	1.41 ± 0.17	3.25 ± 0.35	0.97 ± 0.14	1.05 ± 0.14
22.68	3-Hexenal	689 ± 83	655 ± 77	277 ± 30.5	32.7 ± 2.9	43.02 ± 5.5	173.3 ± 18	177 ± 20	229 ± 34	699 ± 78	1139 ± 122	135.7 ± 14.6	240 ± 26.8	14.1 ± 1.57
22.77	Hexanal	1165 ± 137	764 ± 84	644 ± 96	672 ± 75	352 ± 28	697 ± 73	731 ± 107	601 ± 80	141.5 ± 14	288 ± 33	231 ± 25.8	338 ± 36.3	558 ± 49
24.25	3-Methylhexenylether	0.45 ± 0.06	ND	0.43 ± 0.05	0.38 ± 0.05	ND	ND	ND	ND	ND	4.61 ± 0.51	2.36 ± 0.24	0.49 ± 0.06	0.23 ± 0.03
25.41	2-Hexenal	2874 ± 345	1774 ± 189	2428 ± 254	1874 ± 195	1329 ± 125	3434 ± 377	2967 ± 322	2951 ± 317	1531 ± 144	1602 ± 154	1802 ± 197	2079 ± 246	1047 ± 99
25.49	3-Hexenol	41.6 ± 3.3	13.7 ± 1.1	23.08 ± 2.1	39.5 ± 3.9	5.24 ± 0.44	63.2 ± 5.2	86.7 ± 7.8	39.5 ± 3.9	263 ± 24.3	22.2 ± 2.2	23.9 ± 2.24	14.4 ± 1.38	10.9 ± 0.78
25.84	2-Hexenol	295 ± 30	101.3 ± 10	354 ± 35	354 ± 32	82.8 ± 7.4	524 ± 55	513 ± 54	224.2 ± 22	446 ± 33	182.3 ± 18	139 ± 12.2	348 ± 44	65.6 ± 6.8
27.01	2-Heptanone	ND	0.74 ± 0.09	0.48 ± 0.07	0.56 ± 0.06	0.2 ± 0.02	ND	1.47 ± 0.21	0.84 ± 0.11	1.43 ± 0.21	0.5 ± 0.06	0.73 ± 0.09	0.45 ± 0.05	1.04 ± 0.11
29.71	α-Pinene	ND	ND	ND	3.65 ± 0.47	ND	0.41 ± 0.06	ND	ND	3.64 ± 0.41	0.91 ± 011	ND	ND	1.64 ± 0.22
30.05	2-Heptenal	4.2 ± 0.6	3.49 ± 0.42	4.86 ± 0.8	0.9 ± 0.11	2.53 ± 0.4	4.73 ± 0.66	5.25 ± 0.71	2.78 ± 0.33	4.72 ± 0.56	0.59 ± 0.08	0.97 ± 0.15	0.9 ± 0.11	2.41 ± 0.32
31.87	Octanal	2.79 ± 0.3	4.29 ± 0.34	4.03 ± 0.3	1.47 ± 0.12	2.17 ± 0.17	5.68 ± 0.62	4.83 ± 0.43	5.14 ± 0.39	6.86 ± 0.57	1.77 ± 0.16	2.58 ± 0.27	0.84 ± 0.07	11.1 ± 0.94
33.49	Limonene	ND	1.93 ± 0.25	1.37 ± 0.16	4.06 ± 0.63	2.87 ± 0.33	3.81 ± 0.57	18.52 ± 2.4	4.98 ± 0.64	24.8 ± 2.9	2.97 ± 0.41	3.31 ± 0.41	1.73 ± 0.24	0.68 ± 0.11
36.01	Nonanal	25.8 ± 1.8	16 ± 1.4	15.64 ± 1.2	5.71 ± 0.55	8.26 ± 0.74	24.9 ± 2.2	24.8 ± 2.4	15.7 ± 1.5	12.7 ± 1.13	5.48 ± 0.49	6.96 ± 0.61	5.19 ± 0.41	7.32 ± 0.68

Table 1. Continued

Rt (min)	Compound	Toccolana 14	Dritta 15	Dritta 16	Dritta 17	Tondalblea 18	Tondalblea 19	Arbequina 20	Itrana 21	Tortiglione 22	Coratina 23	Raggia 24	Nocellara 25
4.20	Acetaldehyde	36.5 ± 4.2	14.63 ± 1.7	2.91 ± 0.24	5.02 ± 0.45	2.07 ± 0.23	51.7 ± 6.12	33.9 ± 4.07	8.52 ± 0.91	23.8 ± 2.56	16.7 ± 1.41	2.48 ± 0.34	11.04 ± 1.65
4.28	Methanol	2371 ± 245	2721 ± 256	1772 ± 186	2400 ± 235	1489 ± 163	2541 ± 244	3115 ± 325	879 ± 91.5	2463 ± 285	1645 ± 178	1461 ± 167	3010 ± 312
5.05	Methylformate	30.1 ± 3.3	ND	8.87 ± 0.97	ND	ND	32.1 ± 3.1	25.83 ± 2.9	2.37 ± 0.27	22.3 ± 2.45	12 ± 1.34	ND	ND
5.91	Ethanol	2316 ± 215	3636 ± 265	776 ± 40	1757 ± 125	1573 ± 131	2878 ± 267	5374 ± 478	1308 ± 117	3401 ± 272	1740 ± 96	1308 ± 115	4944 ± 465
6.87	2-Propenal	29.7 ± 1.96	5.5 ± 0.27	0.65 ± 0.02	2.39 ± 0.1	4.44 ± 0.42	7 ± 0.67	15.65 ± 1.38	6.25 ± 0.43	11.81 ± 0.77	4.43 ± 0.15	2.3 ± 0.18	6.4 ± 0.58
7.08	Acetone	552 ± 60	145.5 ± 13.8	197 ± 20.5	124.8 ± 11.8	55.7 ± 5.7	320 ± 36.8	1009 ± 110	486 ± 51	142.4 ± 16.1	89.3 ± 7.6	243.6 ± 26.8	183.6 ± 20.4
7.67	Propanal	15.24 + 1.44	6.59 ± 0.31	5.92 ± 0.24	8.21 ± 0.54	6.21 ± 0.71	4.11 ± 0.44	42.88 ± 4.11	25.4 ± 2.5	4.98 ± 0.55	16.1 ± 0.68	5.01 ± 0.61	29.17 ± 2.77
8.47	Methylthiomethane	ND	0.19 ± 0.01	0.58 ± 0.02	ND	1.62 ± 0.11	23.57 ± 1.45	ND	ND	8.51 ± 0.57	10.46 ± 0.43	ND	33 ± 2.64
8.81	Methylacetate	31.3 ± 2.65	41.6 ± 2.12	18 ± 0.82	156.6 ± 10.9	41.9 ± 2.44	353 ± 28	242.4 ± 13.6	11.5 ± 0.92	152.2 ± 12.2	101.6 ± 6.1	26 ± 1.43	205.1 ± 18.1
9.33	Dimethylsulfone	0.96 ± 0.06	1.65 ± 0.11	1.21 ± 0.09	3.92 ± 0.31	ND	ND	1.92 ± 0.16	2.63 ± 0.21	2.01 ± 0.12	1.49 ± 0.09	3.6 ± 0.29	ND
10.13	Isobutanal	71.2 ± 8.12	40 ± 4.42	40.9 ± 3.9	34.08 ± 3.61	13.9 ± 1.45	235.6 ± 26.7	92.5 ± 10.2	39.3 ± 4.33	188.7 ± 20.2	125.6 ± 10.9	68.8 ± 7.23	49.35 ± 5.24
10.61	2-Butenal (crotonal)	20.5 ± 1.67	6.09 ± 0.37	13.3 ± 0.93	19.07 ± 1.71	1.98 ± 0.18	10.64 ± 0.78	4.98 ± 0.42	11.14 ± 1.01	5.19 ± 0.47	5.28 ± 0.45	4.3 ± 0.34	3.28 ± 0.26
11.75	2-Butenone	3.21 ± 0.41	1.39 ± 0.18	0.72 ± 0.07	1.26 ± 0.14	0.91 ± 0.13	2 ± 0.28	3.63 ± 0.58	1.38 ± 0.19	1.31 ± 0.18	0.66 ± 0.08	0.9 ± 0.14	ND
11.87	Butanal	12.7 ± 1.78	2.64 ± 0.32	1.07 ± 0.11	1.94 ± 0.25	1.37 ± 0.16	3.05 ± 0.38	7.72 ± 1.23	3.38 ± 0.51	1.94 ± 0.28	1.8 ± 0.16	0.84 ± 0.09	ND
12.22	2-Butanone	89 ± 9.12	11.5 ± 1.25	20.2 ± 1.88	83.54 ± 8.8	9.58 ± 1.03	17.5 ± 1.89	64.4 ± 6.9	35.6 ± 3.8	12.54 ± 1.35	39.3 ± 4.15	15.52 ± 1.78	28.04 ± 2.76
12.54	2-Butanol	1.14 ± 0.17	0.7 ± 0.09	0.23 ± 0.03	ND	0.55 ± 0.08	2.89 ± 0.37	1.95 ± 0.29	0.88 ± 0.12	ND	ND	0.37 ± 0.04	4.03 ± 0.61
12.91	2-Methyl-3-buten-2-ol	1.62 ± 0.24	3.42 ± 0.36	6.41 ± 0.98	3.32 ± 0.46	1.4 ± 0.22	5.28 ± 0.69	2.33 ± 0.33	8.34 ± 0.92	4.28 ± 0.64	3.6 ± 0.43	9.56 ± 1.15	6.04 ± 0.72
13.07	Ethyl acetate	247.8 ± 26.8	75.84 ± 8.07	18.16 ± 2.72	53.2 ± 6.9	136 ± 15.4	336 ± 35	423 ± 46	57.3 ± 6.12	179 ± 18.3	150.7 ± 13.8	20.45 ± 2.22	242.2 ± 26.8
13.77	Isobutanol	60.6 ± 7.9	14.25 ± 1.58	22.88 ± 3.56	38.6 ± 4.6	18.5 ± 2.8	78.7 ± 9.44	138 ± 17.7	24.9 ± 3.23	66.6 ± 9.32	77.2 ± 8.8	23.16 ± 3.27	82.1 ± 11.8
15.27	3-Methylbutanal	188.1 ± 19.4	110 ± 12.4	49.1 ± 5.22	86.2 ± 8.9	28.6 ± 3.11	386 ± 36.4	168 ± 18.4	48.1 ± 5.12	268.6 ± 28.8	146 ± 13.8	115 ± 12.5	177.2 ± 18.6
15.81	2-Methylbutanal	194.7 ± 21.7	104.4 ± 10	57.4 ± 6.13	112.4 ± 12.8	32.2 ± 3.75	287 ± 32.5	328 ± 33.4	53.3 ± 5.88	236.7 ± 26.7	126 ± 13.4	94.5 ± 11.5	140 ± 16.7
16.69	1-Penten-3-ol	190.7 ± 20.5	114.2 ± 9.8	121.8 ± 11.2	383 ± 40	134.6 ± 11.6	290 ± 27.4	429 ± 38	122.3 ± 11.3	225.8 ± 23.8	230.4 ± 22.4	190 ± 17.9	511 ± 48
16.93	2-Pentanone	107.7 ± 9.45	198 ± 21.3	707 ± 102	581 ± 68	320.9 ± 33.8	512 ± 56	263 ± 24.7	142.2 ± 16.8	285 ± 35.7	237.7 ± 25.5	255.7 ± 33.6	479 ± 54
17.15	Isooctane (i.s.)	–	–	–	–	–	–	–	–	–	–	–	–
17.49	Pentanal	342 ± 38.2	520 ± 76	382 ± 42	480 ± 66	261 ± 35.6	570 ± 64	694 ± 75	361 ± 42	316 ± 34.2	341 ± 41	283.5 ± 32.5	730 ± 84
17.67	3-Pentanone	101.5 ± 12.1	16 ± 2.31	39.8 ± 4.23	232 ± 26	7.26 ± 1.02	16.28 ± 1.82	330 ± 35.7	21.98 ± 2.45	12.7 ± 1.31	21.9 ± 2.36	12.62 ± 1.38	13.63 ± 1.45
19.38	3-Methyl-1-butanol	101 ± 7.1	25.5 ± 1.52	23.9 ± 1.34	70 ± 5.58	29.7 ± 2.45	50.3 ± 4.73	89 ± 7.9	52.6 ± 4.9	63.1 ± 5.87	91.1 ± 8.9	34.9 ± 3.12	67.8 ± 6.22
19.61	2-Methyl-1-butanol	39.3 ± 4.33	17.5 ± 2.09	22.38 ± 3.22	40.3 ± 5.53	17.97 ± 1.92	29.8 ± 3.87	72.7 ± 10.2	28.2 ± 3.25	33.9 ± 3.67	45 ± 5.76	17.34 ± 1.89	44.5 ± 6.23
21.02	1-Pentanol	5.88 ± 0.48	2.73 ± 0.34	13.8 ± 1.52	17.9 ± 1.86	1.21 ± 0.09	8.21 ± 0.78	11.21 ± 0.98	5.02 ± 0.43	4.77 ± 0.41	6.07 ± 0.7	5.65 ± 0.47	5.55 ± 0.53
21.22	2-Pentenol	26.4 ± 2.47	10.23 ± 0.88	26.8 ± 2.54	104.4 ± 9.8	21.8 ± 2.45	40.6 ± 3.89	51.8 ± 5.34	41.9 ± 4.76	36.6 ± 3.45	58.63 ± 6.15	65.8 ± 7.29	82.1 ± 8.47
22.24	2-Hexanone	ND	0.76 ± 0.08	1.27 ± 0.19	2.09 ± 0.28	ND	0.58 ± 0.08	1.17 ± 0.14	0.64 ± 0.09	0.71 ± 0.09	0.9 ± 0.13	0.89 ± 0.14	1.91 ± 0.28
22.68	3-Hexenal	20.8 ± 2.24	100.6 ± 9.88	49.8 ± 5.22	73.1 ± 7.9	1352 ± 162	2966 ± 396	102.4 ± 12.6	184.7 ± 24.4	252 ± 34.3	128.3 ± 14.7	293 ± 42.7	3303 ± 398
22.77	Hexanal	855 ± 84	858 ± 96	636 ± 83	660 ± 76	370 ± 36	447 ± 41.6	1487 ± 105	370 ± 34	225 ± 18.1	685 ± 84	645 ± 61	476 ± 43
24.25	3-Methylhexenylether	ND	ND	0.31 ± 0.04	10.51 ± 1.25	21.96 ± 2.43	13.14 ± 1.78	4.84 ± 0.62	7.53 ± 0.91	ND	0.69 ± 0.1	2.88 ± 0.46	12.58 ± 1.64
25.41	2-Hexenal	1957 ± 184	2933 ± 348	1530 ± 173	2846 ± 328	1033 ± 97	541 ± 53.6	2473 ± 234	1614 ± 168	1890 ± 178	2152 ± 234	2485 ± 234	1580 ± 146
25.49	3-Hexenol	63 ± 5.8	26.24 ± 2.75	46.9 ± 4.9	73.8 ± 7.05	50.5 ± 4.36	129 ± 11.4	44.78 ± 4.2	42.7 ± 3.9	44.24 ± 4.23	92.7 ± 8.84	251.2 ± 23.6	831 ± 77
25.84	2-Hexenol	236.5 ± 24.7	205.3 ± 18.9	268 ± 28.6	606 ± 79	74.4 ± 7.32	40.6 ± 4.87	403 ± 28.1	295 ± 27.3	142.6 ± 11.6	191 ± 17.6	185.7 ± 16.4	154 ± 12.7
27.01	2-Heptanone	1.49 ± 0.17	0.6 ± 0.07	0.92 ± 0.14	0.68 ± 0.08	0.31 ± 0.04	1.41 ± 0.16	1.04 ± 0.12	0.8 ± 0.12	0.42 ± 0.04	1.24 ± 0.16	3.83 ± 0.53	1.81 ± 0.21
29.71	α-Pinene	2 ± 0.28	1.03 ± 0.12	ND	ND	ND	ND	ND	ND	ND	3.48 ± 0.52	ND	ND
30.05	2-Heptenal	4.47 ± 0.64	4 ± 0.6	4.65 ± 0.58	5.02 ± 0.75	0.59 ± 0.08	5.52 ± 0.67	4.92 ± 0.68	2.11 ± 0.27	1.68 ± 0.25	1.59 ± 0.24	2.55 ± 0.31	3.29 ± 0.49
31.87	Octanal	11.74 ± 1.12	3.62 ± 0.33	2.04 ± 0.19	2.92 ± 0.25	13.7 ± 1.24	8.41 ± 0.74	8.58 ± 1.18	8.21 ± 0.78	24.7 ± 2.34	21.63 ± 1.79	8.18 ± 0.65	19.45 ± 1.81
33.49	Limonene	8.86 ± 1.06	2.8 ± 0.31	1.19 ± 0.18	3.06 ± 0.39	0.31 ± 0.04	9.48 ± 1.08	1.88 ± 0.21	2.02 ± 0.26	ND	0.65 ± 0.08	2.77 ± 0.41	5.38 ± 0.64
36.01	Nonanal	12.2 ± 0.96	7.55 ± 0.61	10.18 ± 0.11	13.79 ± 1.24	4.79 ± 0.57	16.3 ± 1.45	16.1 ± 1.45	13.6 ± 1.34	3.71 ± 0.48	6.39 ± 0.45	6.25 ± 0.67	18.21 ± 1.65

Isooctane was used as the internal standard (i.s.) (0.02 µL is equivalent to 13.8 µg).
Values are mean ± standard deviation ($n = 3$).
ND, not detected; Rt, retention time.

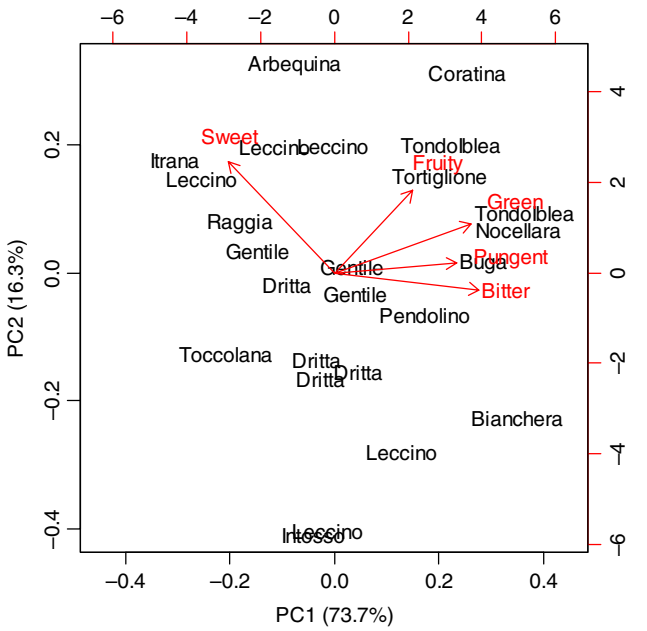

Figure 1. Biplot (principal component analysis analysis) of the sensory descriptors.

of panel evaluations. The analysis showed high positive correlation between oil from Leccino cultivar and sweet sensation while oils from Tonda Iblea and Tortiglione seem correlated with fruity and green properties; also the Nocellara variety seems correlated with green properties while Buga varieties with pungent and bitter sensation. Buga, Bianchera and Pendolino cultivars show a positive correlation with bitter properties.

The PLS analysis was conducted with the aim of correlating the sensorial data with the compounds present in the volatile fraction of the analysed olive oils. Cross-validation was used to select the number of components of the model, which were two. The two components accounted for 52% of total variation of sensory data and 36% of analytical data. The sensory variables evaluated in PLS analysis proved to be sweet, fruity, bitter, pungent and green. The estimates of the coefficients relating each compound to the sensory descriptors are reported in Fig. 2. Given the high correlations among the sensory variables (see principal component analysis results), the estimated coefficients are very similar (with opposite sign for sweet) for all the descriptors, and the corresponding plots in the plot are stacked. For this reason it is better to evaluate the effect of analytical compounds on sweet and green characteristics, the last one intended in a broad sense to include also fruit, pungent and bitter.

Sixteen volatile compounds seem related to the positive odour properties. In particular, as stated earlier, the substances may be gathered into two groups of positive volatiles as sweet or green type. The PLS analysis has shown that the positive attributes of virgin olive oil are divided into two separated groups as sweet or green types. Fruity, bitter and pungent compounds are correlated with green substances and this property is the opposite of the sweet type.

In particular, eight compounds were correlated with sweet properties: among them 2-heptanone was found: its low concentration, in a range from 0 to 3.83 μg kg^{-1}, correlated with literature threshold value (300 μg kg^{-1}),[21] indicates a probable minor

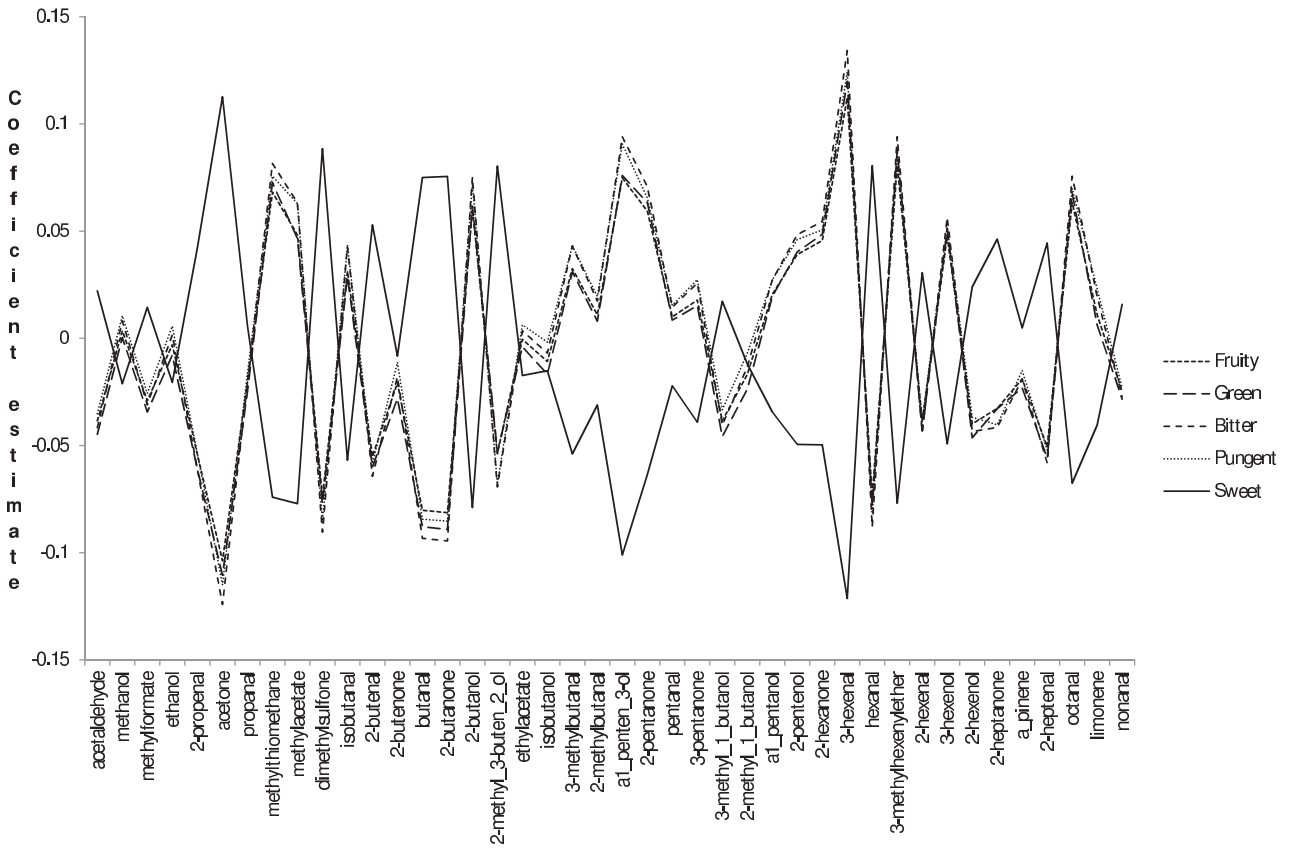

Figure 2. Partial least squares (PLS) regression coefficients relating sensory descriptors to chemical compounds.

impact of the compound in odour properties of the samples. 3-methyl-1-butanol, in a range from 23.9 to 172.4 mg kg^{-1}, and ethylacetate, in a range from 18 to 423 mg kg^{-1}, also have a high level of positive correlation with sweet attributes. The literature threshold value related to 3-methyl-1-butanol (100 μg kg^{-1})[22] has shown a possible major impact of this compound on odour properties of virgin olive oil in comparison with ethyl acetate (threshold value 940 μg kg^{-1}). The concentration of acetaldehyde, in a range from 2 to 161 μg kg^{-1}, correlated with a low literature threshold value (0.22 μg kg^{-1}), may be very important for the characterisation of the positive attributes of virgin olive oil. Besides, another two ketones seem correlated with sweet properties: acetone, in a range from 55.7 to 1008 μg kg^{-1} and 2-butanone, in a range from 9.58 to 109 μg kg^{-1}. However, since the literature threshold value for 2-butanone is very high (40 000 μg kg^{-1}), no important impact on odour properties should be expected. Butanal, in a range from 0 to 12.7 μg kg^{-1}, and dimethylsulfone, in a range from 0 to 5.39 μg kg^{-1}, seem correlated with sweet attributes. The purge-and-trap technique performed at room temperature has permitted the extraction of particular compounds that seem correlated with sweet sensation. The high content of acetone and the presence of dimethylsulfone in the volatile fraction, in addition to the content of 3-methyl-1-butanol and acetaldehyde, could be very important for the characterisation of sweet sensorial sensation.

In the case of 'green' properties, eight compounds were correlated with sensory evaluation. Three aldehydes, hexanal, in a range from 141 to 1487 μg kg^{-1} (threshold 80 μg kg^{-1}), (*Z*)-3-hexen-1-al, in a range from 14 to 3303 μg kg^{-1} (threshold 3 μg kg^{-1}) and isobutanal, in a range from 13.9 to 262 μg kg^{-1}, were identified. The concentration ranges of hexanal and (*Z*)-3-hexen-1-al and low threshold values, showed the high impact on odour properties of these substances. Additionally, two alcohols, (*E*)-2-hexen-1-ol, in a range from 40 to 606 μg kg^{-1} (threshold 5000 μg kg^{-1}) and (*Z*)-3-hexen-1-ol, in a range from 5.24 to 263 μg kg^{-1} (threshold 6000 μg kg^{-1}) were identified as green compounds, in good agreement with literature.[23] On the basis of their lower threshold values, they probably have minor importance on flavour characteristics, compared to the aldehydic compounds. Moreover, PLS analysis showed that 3-methylhexenylether, in a range from 0 to 21.96 μg kg^{-1}, methylacetate, in a range from 18 to 389 μg kg^{-1} and methylthiomethane, in a range from 0 to 73.7 μg kg^{-1}, may be correlated with green attributes. The extraction of samples with purge-and-trap technique performed at room temperature has permitted the identification of these compounds. In particular, the impact on odorous properties of sulfur compounds should be very important, as shown by the correlation of Tonda Iblea and Nocellara of the Belice samples and green attributes on sensorial biplot (Fig. 1).

CONCLUSIONS

The particular analytical technique used to characterise the volatile fraction of olive oil could be an interesting method to obtain a 'true' aromatic profile very similar to natural olfactory perception, without artefact formation or problems related to saturation and competition phenomena. Therefore, it is possible to compare the chemical analysis of the samples to the sensory evaluation. The chemometric approach showed a possible correlation between mono-cultivar oil and sensory sensation and between chemical compounds and sensory properties. Sixteen volatile compounds with positive impact on odour properties were extracted and identified. PLS showed that the volatile fraction of extra virgin olive oils is generally characterised as sweet or green type. Eight compounds were correlated with sweet properties, while 'green' sensation was given by eight other different substances. Positive sensory characteristics are associated to C5 and C6 compounds. The most abundant compounds contributing positively to the aroma profile of virgin olive oil are the C5 and C6 aldehydes and alcohols.

The preliminary data obtained in this study have shown that with the particular analytical tool proposed, it has been possible to correlate chemical compounds to the true aromatic profile of olive oils. In order to improve this, it will be necessary to analyse a number of samples of good quality produced considering other parameters that influence the volatile composition, such as extraction processes and the period of harvesting.

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