NEW FORMULATIONS OF OLIVE-BASED PÂTÉ: DEVELOPMENT AND QUALITY

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ABSTRACT

The aim of this research was the chemical, microbiological, and sensory characterization of new ingredient formulations of olive-based pâtés, since few studies are present in the literature regarding table olive-based processed products. Three ingredient formulations were selected by a consumer test on the basis of the scores of *odour* and *taste* descriptors, higher than 6 (linear scale 0-10 cm). The chemical and sensory analyses allowed to clearly differentiate all ingredient formulations on the basis of both composition and volatile profile. Microbiological data corresponded to levels usually detected for similar products and excluded the presence of pathogens. Finally, no off-flavour was perceveid in the tested formulations.

1. INTRODUCTION

Table olives (*Olea europaea* L.) are one of the most important traditional fermented vegetables in the Western world (BLEVE *et al.*, 2015) and, similarly to olive oil, one of the most characteristic components of the diet in Mediterranean countries. The world production of table olives has shown a steady increase for the last 20 years and is mainly concentrated in Spain, Turkey, Egypt, Syria, Morocco, Italy, and Greece. The International Olive Council (IOC, 2014) estimated that table olive production (2011/2012 season) was above 2.4 milliontons.

According to the Trade Standard Applying to Table Olives (IOC, 2004), table olives are prepared from sound olive fruits whose volume, shape, flesh-to-stone ratio, firmness, and taste make them particularly suitable for processing. Moreover, table olives have to be treated to remove bitterness by natural fermentation or by heat treatment, with or without the addition of preservatives.

Table olives have been attracting increasing interest, due to their postulated health benefits, that seem to be intrinsically linked to the high monounsaturated fatty acid content, as well as to their important antioxidant capacity, antimicrobial activity, and protection against mycotoxin effects due to minor constituents like tocopherols and phenolic compounds (MALHEIRO *et al.*, 2011).

Table olives consumption is greatly varied: the fruits, conveniently processed, can be served as an appetizer or as a complement to salads, pasta, pizza, fish, and meat. Even bread can be prepared by adding green/black olives to the dough (SABATINI *et al.*, 2009; LANZA, 2012).

As reported by IOC (2004), table olives consumption showed an increase primarly attributable to the marketing efforts by manufacturers essentially aimed at the introduction of new products, to satisfy the growing consumers' awareness of their health benefits. In this context, the table olives characterized by defects in terms of size and/or shape, unsuitable to be marketed as such, could represent the base for the preparation of new commercial products among which olive-based pâtés.

The term "pâté" indicates a processed product that has important gastronomic tradition and good sensory properties with a coarse texture (ÜNLÜSAYIN *et al.*, 2007) in which the main ingredients are more or less finely ground and mixed with various ingredients, considered essential for their binding capacity.

With respect to other types of vegetable pâtés – for example tomato-based pâtés, characterized by a complex ingredient formulation (the starting vegetable is usually associated with other kinds of ingredients, such as mushrooms, eggplants, peppers, oil, spices, and herbs) – usually commercial olive-based pâtés contain only table olives and olive oil.

Table olives have been studied from microbiological (PEREIRA *et al.*, 2008; TASSOU *et al.*, 2002; HURTADO *et al.*, 2008; ARROYO-LÓPEZ *et al.*, 2008; PANAGOUA *et al.*, 2008; CAMPANIELLO *et al.*, 2005), chemical (MONTAŇO *et al.*, 2003; APONTE *et al.*, 2010; ROMEO *et al.*, 2010; PASQUALONE *et al.*, 2014), and sensory points of view (SABATINI and MARSILIO, 2008; PÉREZ *et al.*, 2007). However, no studies are present in the literature regarding table olive-based processed products, except for a study carried out by ALVARENGA *et al.* (2012).

On the basis of these considerations, the aim of this study was the development of new formulations of olive-based pâtès to satisfy more dynamic, complex and differentiated consumer demands for traditional and functional foods. It is crucial to consider food safety as well as nutritional, sensory and commercial qualities. In this context sensory, microbiological, and chemical properties of olive-based pâtès were reported.

2. MATERIALS AND METHODS

2.1. Sampling

The trials were carried out utilizing cv. *Bella di Cerignola* table olives, debittered by the Spanish method (PASQUALONE *et al.*, 2014), purchased at local retailers without defects. The experimental plan required that the olives represent at least 50% of the total ingredient formulation, while the choice of the other ingredients was made through preliminary tasting sessions that were designed to assess which combinations were judged the best among different ingredients. Extra virgin olive oil (EVOO) of Coratina cultivar was used in the experimental trials.

A total of six formulations (F1, F2, F3, F4, F5, F6) were evaluated:

- F1, table olives (500 g kg^{-1}), EVOO (170 g kg^{-1}), sweet shelled almonds (165 g kg^{-1}), water (165 g kg^{-1});
- F2, table olives (640 g kg^{-1}), EVOO (100 g kg^{-1}), olive-oil tuna (130 g kg^{-1}), dried tomatoes (130 g kg^{-1});
- F3, table olives (770 g kg^{-1}), EVOO (155 g kg^{-1}), zucchini (75 g kg^{-1});
- F4, table olives (750 g kg^{-1}), EVOO (50 g kg^{-1}), dried tomatoes (50 g kg^{-1}), red peppers (50 g kg^{-1}) eggplants (50 g kg^{-1}), mushrooms (*Pleurotus eryngii*) (50 g kg^{-1}), capers (1 No.);
- F5, table olives (770 g kg^{-1}), EVOO (150 g kg^{-1}), salted anchovies (40 g kg^{-1}), red onion (40 g kg^{-1}), leaves of arugula (2-3 No.), drop balsamic vinegar (5 No.);
- F6, table olives (750 g kg^{-1}), EVOO (130 g kg^{-1}), salted anchovies (60 g kg^{-1}), red onion (60 g kg^{-1}).

Before the olive-based pâtés production, some raw materials were subjected to preliminary treatments: table olives were washed and pitted; dried tomatoes and mushrooms were blanched in boiling water or water/vinegar (1:1 v/v), respectively, for two minutes; zucchini, red peppers, and eggplants were roasted.

All ingredients were mixed by means of a homogenizer (Waring LB 20 ES, Rome, Italy) until obtaining a homogeneous creamy paste (about 5 minutes at 12,000 rpm). After mixing, the product was transferred and packed in plastic boxes having the capacity of 100 g.

2.2. Consumer test

A consumer test was conducted for the six different formulations. A total of 90 people (mean age 27 years, range 17-60 years, 45 males and 45 females) participated in the consumer test, which was performed within 4 hours from pâté production.

The participants were selected among people who regularly consumed vegetable pâtés (i.e. 1-4 times a month). An alpha-numeric code was assigned to each pâté, served in white plastic cups (about 10 g). After trying, several different palate cleansers to avoid carry-over effects and adaptation to sensory stimuli, mineral water and a 1-minute break between samples were chosen. Before starting the evaluation of products, the investigator read aloud the instructions to the participants. Each subject was asked to fill a sensory evaluation sheet composed of a first part regarding personal information (age and sex), and a second part that included a continuous 10 cm-line on which consumers expressed an acceptability judgment for *odour pleasant* and *taste pleasant* descriptors, respectively. Testing was performed at room temperature (20 °C) with artificial lighting, simulating daylight.

2.3. Sensory analysis

On the basis of the results of consumer test, the three most appreciated pâté were submitted to a descriptive sensory analysis by a trained panel of assessors. The first step has provided the identification of the sensory descriptors, in order to develop a common vocabulary for the description of the sensory attributes and to familiarize with scales and procedures. Each attribute term was extensively described and explained to avoid any doubt about the relevant meaning. On the basis of the citation frequency (>60%), eleven descriptors were selected and related to the rheological characteristics (consistency and phase separation), visual characteristics (brightness and colour homogeneity), taste (bitter, acid, sweet, salt), and flavour (olive flavour and off-flavour). Each descriptor was scored on a non-structured line scale of 10 cm.

A panel of eight assessors, aged between 25 and 50 years, was trained through preliminary sessions to ensure that each panelist interpret the same descriptor in the same way. The same product was also subjected several times, without their knowledge, to repeatedly tasting to assess the ability of panelists to detect the intensity of each descriptor always in the same way. The panel consisted of teachers and students, and all sensory tests were performed in the sensory laboratory of Food Science and Technology section of Bari University, which fulfills the requirements of the international standards (ISO, 1988).

During the evaluation phase, the panelists were seated in private booths equipped with air conditioning and under incandescent/fluorescent light. The sample presentation order was randomized for each panelist. The samples, identified by an alpha-numeric code, were served to each panelist in plastic cups at room temperature, and tap water was provided between samples to cleanse the palate.

Samples were analyzed in duplicate.

2.4. Microbiological analysis

Microbiological analysis included the determination of contaminating micro-organisms and pathogens (Coliforms, *Salmonella* spp., *Listeria monocytogenes* and *Escherichia coli*). All cultural media, supplements, and diagnostic kits were provided by Oxoid (Basingstoke, UK).

Coliforms were determined by count in plates of selective medium Violet Red Bile Glucose Agar (38.5 g/L in distilled water boiled for 2 min), seeding 1 mL of decimal dilutions for inclusion and incubating the plates at 30 °C for 24 h (ANON, 1996).

The counting was done considering only the characteristic colonies (dark red with diameter > 0.5 mm, with or without the surrounding precipitate), while the others were submitted to the confirmation. This was made inoculating 3-5 colonies with a loop in tubes of sterile broth of Brilliant Green Lactose then incubated at 30 °C for 24 h. All colonies developed in the culture broth with gas production were included in the count of coliform. The monitoring of *L. monocytogenes* (ANON, 1996) consists of several stages: i) the primary selective enrichment: 25 g of sample were spiked with 225 mL of Half Fraser and the incubated at 30 °C for 24-48 h; ii) secondary selective enrichment: 0.1 mL of the primary enrichment culture were incubated in 10 mL of medium Fraser Broth at 37 °C for 24-48 h; iii) isolation: a loopful of enrichment culture was streaked on distinct plates of Oxford Agar and Palcam Agar, incubated at 37 °C for 24-48 h (in microarofilia conditions with 5-12% CO_2, 5-15% O_2, 75% N_2 only for Palcam agar plates); iv) confirmation and identification: by each isolation medium were taken at least 5 characteristic colonies to perform subculture by streaking on the Tryptone Soy Yeast Extract Agar, incubated at 37 °C for 24-48 h. The identification was performed with biochemical tests of catalase, Gram-

stain and hemolysis on plates of Blood Agar Bases supplemented with defibrinated sheep blood after 24-48 h of incubation at 37 °C.

For the determination of *E. coli*, 25 g of each pâté were homogenized in 225 mL of the solution of Tryptone Soy Broth and incubated at 37 °C for 18 h under stirring (150 rpm). From each crop, inocula of 0.1 mL were made through smear on MacConkey Sorbitol Agar enriched with Cefixime-Tellurite Supplement. The plates, produced in triplicates, were incubated at 35 °C for 20-22 h before counting the probable colonies of E. coli 0157:H7; identification was made with the use of E. coli O157 Test Kit (ABDUL-RAOUF *et al.*, 1993). The results were expressed as cfu/g of sample.

2.5. Chemical analysis

The measurements of pH were conducted by using a Basic 20 pH meter (Crison Instruments S.A., Barcelona, Spain) provided with a conductivity penetration probe (Codito 50 10T, Crison Instruments S.A., Barcelona, Spain) and a temperature compensator.

Moisture content was estimated by drying the samples at 105±5 °C, and ash content by incineration, both until constant weight (AOAC, 2000). Fat content was determined by Soxhlet extraction with 40-60 °C diethyl ether for 6 hours, followed by evaporation of the solvent (IUPAC, 1979). Protein content was determined by Kjeldahl method (N × 6.25) (AOAC, 2000). Carbohydrate content was estimated by subtracting the weight of the other components to the total weight.

2.6. Headspace analyses

Volatile compounds were extracted by solid-phase micro-extraction (SPME) and analyzed by a gas-chromatographic system equipped with mass spectrometer (GC-MS). In particular, an aliquot of sample (1 g ± 0.05) was placed inside 12-mL glass vials, closed by silicone/PTFE septa and an aluminum seal. The pâté sample was homogenized for 2 min using a laboratory vortex shaker. Before extraction, stabilization of the headspace in the vial was achieved by equilibration for 5 min at 40 °C. The extraction was performed by exposing a 75-μm Polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR) fiber (Supelco, Bellefonte, Pa., USA) in the headspace of the sample at 40 °C for 15 min. When the extraction process was completed, the fiber was removed from the vial and desorbed in the injection port of the GC in a splitless mode. The GC-MS instrumentation included an Agilent 6850 gas-chromatograph (Milan, Italy) equipped with an Agilent 5975 single quadruple mass-spectrometer. Compounds were resolved on a HP-Innowax (20 m × 0.18 mm, 0.18 μm film thickness) polar capillary column (Agilent, Milan, Italy) under the following conditions: injector temperature, 220 °C; helium as the carrier gas at a flow rate of 15 mL/min for 7 min; oven temperature was at 40 °C/0.70 mL/min (linear speed of 36 cm/sec), then increased at 18 °C/min up to 180 °C, then increased at 20 °C/min up to 220 °C. The mass spectrometer was operated in the electron impact mode (electron energy = 70 eV) and the ion source temperature was 250 °C. The mass range was m/z 20-250. The volatile compounds were identified by comparison with the mass spectra present in the NIST and Wiley libraries, quantified and expressed in terms of integrated area.

2.7. Statistical analysis

The results were expressed as mean and standard deviation of three different trials and all the analytical determinations were carried out in triplicate. Analysis of variance (one-way ANOVA) was carried out on the chemical and microbiological analyses, whereas two-way

ANOVA was used on sensory analysis, considering *formulation* and *panelist* as independent variables. Significant differences among the values of all parameters were determined at $p \le 0.05$. All data were processed by the XLStat software (Addinsoft SARL, New York, NY, USA).

3. RESULTS AND DISCUSSION

Table 1 shows the mean values and the results of a statistical analysis (one-way ANOVA) of the scores attributed to *odour* and *taste* during the consumer test performed on six different types of olive-based pâtés. The acceptability of the formulations was evaluated in order to identify the most appreciated, by considering only formulations scored more than 6 on a 0-10 scale.

Table 1. Means values and standard deviation of the results of consumer test performed for the six different ingredient formulations of olive-based pâtés.

Pâtés	Pleasant odour	Pleasant taste
F1	4.55±2.22 [d]	5.19±2.15 [c]
F2	5.16±2.49 [c]	6.42±2.74 [b]
F3	6.01±2.60 [b]	6.62±2.45 [b]
F4	6.50±2.12 [ab]	7.22±2.26 [a]
F5	7.00±2.03 [a]	6.64±2.00 [b]
F6	5.80±2.31 [bc]	6.37±2.21 [b]

a-d, different letters indicate a significant difference at $p \le 0.05$.

The data showed significant differences among all the considered samples. Relatively to *odour* descriptor, scores higher 6, on linear scale 0-10 cm, were observed in F3, F4, and F5 pâtés. The F4 sample showed the highest *taste* score, even if all the other formulations (except F1) were scored more than 6, with no significant differences among them.
The most appreciated formulations in terms of *odour* were characterized by completely different ingredients among them, demonstrating that it is possible to set up several pleasant combinations, assuming that the components are quantitatively well-balanced. In particular, F3 and F4 were characterized by the presence of different vegetables that contributed to make a specific *odour* more intense which would have otherwise been flat if only table olives had been used, as evidenced for F1. Moreover, in the F1 sample probably the use of almonds flattened both the *odour* and the *taste*. F5 had a higher score than F6, although containing similar ingredients. This result could be attributed to a positive effect of additional ingredients, such as balsamic vinegar and arugula, or salted anchovies.
On the basis of the scores obtained for both *odour* and *taste*, three ingredient formulations were selected: F3, F4, and F5. They reached a mean *odour* score of 6.01, 6.50, and 7.00, respectively, and a mean *taste* score of 6.62, 7.22, and 6.64, respectively. These results evidenced a real possibility to market these products.
Table 2 shows the chemical composition of the three selected pâté formulations and the results of one-way ANOVA. The pH level ranged between 4.95 and 6.76, with significantly lower values in F4, due to the use of dried tomatoes and mushrooms (which needed to be blanched in water/vinegar, 1:1 v/v). Higher values of pH observed in the other formulations were due to the use of olives, which underwent the Spanish debittering

method, involving the use of NaOH. Moisture content was higher in F4, due to the use of a greater amount of vegetables, than in F3 and F5. Fat content, on the contrary, was higher in F3 and F5 than in F4 due to the higher amount of olive and oil used in their recipe.

Protein and ash content were significantly higher in F5, probably due to the presence of salted anchovies, whereas carbohydrate content was higher in F4.

Microbiological analyses (Table 3) performed on the selected pâté formulations shown as coliforms and *E. coli* cell density were below the limit indicated in the EC Regulation No 2073/2005 on microbiological criteria for foodstuffs. Significantly higher values were determined in F5, probably due to the use of salted anchovies (PATIR *et al.*, 2006). Biochemical and serological tests on *Salmonella* spp. and *L. monocytogenes* allow to exclude the presence of pathogens, in agreement with the requirements of the above EC Regulation No 2073/2005.

Table 2. Mean values and standard deviation of percent composition of three selected olive-based pâtés.

Pâtès	pH	Moisture	Fat	Proteins	Carbohydrates	Ashes
F3	6.76±0.03[a]	59.65±0.98[b]	31.00±0.20[a]	1.13±0.02[c]	6.86±1.06[b]	1.36±0.11[c]
F4	4.95±0.04[b]	67.72±0.84[a]	21.27±0.44[b]	1.63±0.02[b]	7.37±0.78[a]	2.01±0.15[b]
F5	6.13±0.01[a]	58.94±0.32[b]	31.85±0.40[a]	1.82±0.02[a]	4.94±0.18[c]	2.45±0.19[a]

a-c, different letters indicate a significant difference at $p \leq 0.05$.

Table 3. Mean values (cfu/g) and standard deviation of the results of microbiological analyses of three selected olive-based pâtés.

Samples	*Coliforms*	*Salmonella* spp.	*Listeria monocytogenes*	*Escherichia coli*
F3	<1000 [b]	Not found in 25 g	Not found in 25 g	<100 (not encountered pathogenic strains)
F4	<1000 [b]	Not found in 25 g	Not found in 25 g	<100 (not encountered pathogenic strains)
F5	$(2.0\pm0.2) \times 10^{3}$ [a]	Not found in 25 g	Not found in 25 g	<100 (not encountered pathogenic strains)

a-b, different letters indicate a significant difference at $p \leq 0.05$.
cfu, colony-forming units.

Fig. 1 shows the GC-MS chromatograms related to headspace analysis of F3, F4, and F5 pâtés. It is possible evidence the good peaks separation and the more complex volatile compounds pattern in F4, in which the main volatile compounds were evidenced. In particular, a total of 77 volatile compounds were identified and grouped in relation to the chemical class they belonged to (Table 4). Generally, the volatile compounds of the examined pâtés were affected by the different ingredients used, but the exact contribution of each ingredient to the volatile fraction of pâtés was difficult to point out: in fact, the major volatile compounds identified were shared by different raw materials, as evidenced by their preliminary headspace analysis (data not showed). In particular, the most abundant volatile compound was acetic acid, significantly more represented in F4 than in F3 and F5. The analysis of raw materials evidenced that the abundance of this compound was mainly attributable to the presence of eggplants, capers, dried tomatoes, and mushrooms, the latter blanched in water/vinegar. The use of capers could justify also the preponderance of other carboxylic acids in F4, with respect to F3 and F5, such as hexanoic and heptanoic acids (ROMEO *et al.*, 2007).
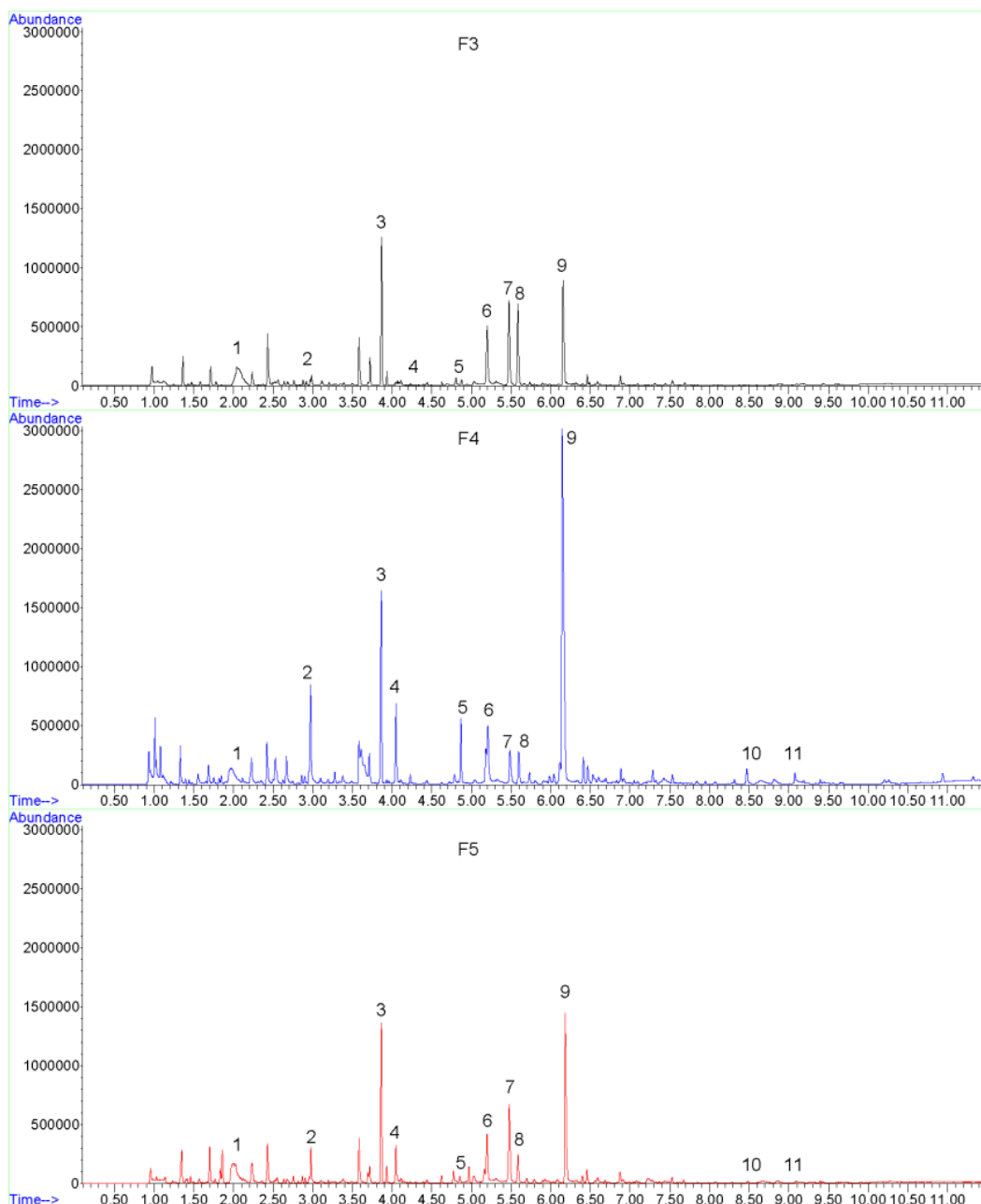
Figure 1. Chromatograms of the headspace of F3, F4, F5 formulations. Number peaks identify the main volatile compounds. 1 = ethanol; 2 = hexanal; 3 = eucalyptol; 4 = 2-hexenal; 5 = 6-methyl-5-hepten-2-one; 6 = 1-hexanol; 7 = (Z)-3-hexen-1-ol; 8 = 2-hexen-1-ol; 9 = acetic acid; 10 = hexanoic acid; 11 = heptanoic acid (Cosmai *et al.*).

The presence of vegetables (eggplants, red peppers, mushrooms, and dried tomatoes) made F4 richer in terpenic compounds more than F3 and F5, such as eucalyptol (contributed by olives and eggplants), D-limonene (from olives, mushrooms, and dried tomatoes), terpinen-4-ol (from olives, dried tomatoes, and eggplants) and linalool (from olives and dried tomatoes). The latter was very abundant also in F5, where it was contributed by olives and arugula. The F4 pâté was also characterized by higher levels of 6-methyl-5-hepten-2-one, related to pungent and green sensory notes. This volatile

derived from the dried tomatoes, being considered as a marker of the lycopene degradation (CREMER and EICHNER, 2000).

Table 4. Mean values of integrated total area of volatile compounds of three selected olive-based pâtés.

Volatile compounds	F3	F4	F5	p-value
Terpenes, phenols, lactones and thiols				
α-Pinene	nd	3.39[a]	2.00[b]	<0.001
β-Pinene	3.59[a]	4.47[a]	2.30[b]	0.010
α-Phellandrene	2.56	nd	nd	<0.001
(+)-4-Carene	1.31	nd	nd	0.085
D-Limonene	17.91[ab]	18.75[a]	12.10[b]	0.095
Eucalyptol	114.19[b]	159.50[a]	127.60[b]	<0.001
2,4-Quinolinediol	nd	4.23[ns]	5.07[ns]	<0.001
Acetophenone	nd	6.94	nd	<0.001
Butyrolactone	3.03[ns]	3.03[ns]	nd	0.005
Benzothiazole	nd	4.67	nd	<0.001
α-Farnesene	2.75[ns]	nd	3.20[ns]	<0.001
2-Ethylphenol	3.30	nd	nd	<0.001
Linalool	8.12[b]	14.34[a]	12.86[a]	<0.001
Terpinen-4-ol	4.53[c]	14.33[a]	10.73[b]	<0.001
Esters				
Methyl acetate	2.34[b]	3.09[b]	4.59[a]	0.006
Ethyl acetate	12.91[b]	13.84[b]	24.23[a]	<0.001
Ethyl butanoate	3.10[a]	1.14[b]	3.04[a]	<0.001
Ethyl 2-methylbutanoate	3.77[b]	2.38[c]	4.84[a]	<0.001
Ethyl 3-methylbutanoate	3.78[c]	6.75[a]	5.11[b]	<0.001
Hexyl acetate	nd	nd	1.04	<0.001
(Z)-3-Hexen-1-ol acetate	3.51[c]	9.76[a]	4.61[b]	<0.001
Methyl benzoate	0.88[b]	3.76[a]	nd	<0.001
Alcohols				
Ethanol	83.65[ns]	80.46[ns]	91.49[ns]	0.363
1-Butanol	nd	51.34[ns]	36.14[ns]	0.007
1-Penten-3-ol	nd	nd	8.80	<0.001
2-Methyl-1-butanol	2.68[ns]	2.26[ns]	2.49[ns]	0.514
3-Methyl-1-butanol	4.59[ns]	4.72[ns]	5.11[ns]	0.376
1-Pentanol	2.85[b]	4.37[a]	3.24[b]	0.001
(Z)-2-Penten-1-ol	4.68[c]	8.00[b]	11.17[a]	<0.001
1-Hexanol	68.98[a]	71.78[a]	54.50[b]	0.001
(Z)-3-Hexen-1-ol	93.94[a]	43.14[b]	95.96[a]	<0.001
(Z)-2-Hexen-1-ol	82.38[a]	36.06[b]	28.96[c]	<0.001
1-Octen-3-ol	1.66[b]	4.85[a]	4.75[a]	0.017
1-Heptanol	0.89[b]	4.69[a]	3.58[a]	0.009
1-Octanol	4.76[b]	7.51[a]	7.65[a]	0.082
Aldehydes				
Propanal	nd	nd	9.38	<0.001
2-Methylpropanal	nd	nd	2.68	<0.001
2,2-Dimethylpropanal-3-pentanone	12.41	nd	nd	<0.001

2-Methylbutanal	nd	5.57^b	10.54^a	<0.001
3-Methylbutanal	nd	9.41^b	26.29^a	<0.001
Pentanal	nd	24.62	nd	<0.001
Hexanal	6.20^c	74.17^a	26.94^b	<0.001
2-Hexenal	2.47^c	70.11^a	28.47^b	<0.001
(E)-2-Heptenal	3.44^b	8.34^a	10.96^a	0.010
Nonanal	nd	4.83^b	12.64^a	<0.001
(E,E)-2,4-Heptadienal	nd	nd	5.36	<0.001
Furfural	nd	9.34^a	2.45^b	<0.001
Benzaldehyde	nd	21.74^a	6.91^b	<0.001
2-Decenal	nd	2.53^b	3.13^a	<0.001
3,5-Dimethylbenzaldehyde	1.36^b	2.92^a	nd	0.035
Ketones				
Acetone	1.34^b	3.35^a	2.73^a	0.009
2-Butanone	2.79^b	4.68^a	2.90^b	0.012
3-Hexanone	nd	nd	1.94	<0.001
6-Methyl-5-hepten-2-one	4.52^b	47.14^a	6.07^b	<0.001
Sulfur compounds				
Dimethyl sulfide	1.11^{ns}	2.16^{ns}	2.05^{ns}	0.112
Dipropyl disulfide	nd	nd	12.55	<0.001
Furans				
2-Pentylfuran	nd	2.05	nd	<0.001
Acids				
Acetic acid	43.21^c	517.62^a	218.83^b	<0.001
Propanoic acid	nd	4.22	nd	<0.001
Pentanoic acid	nd	3.63	nd	0.001
Hexanoic acid	nd	21.94^a	2.33^b	<0.001
Heptanoic acid	nd	10.71^a	2.94^b	<0.001
2-Methyl-2-propenoic acid	nd	2.94	nd	<0.001
Other compounds				
Octane	19.54^{ns}	20.45^{ns}	26.40^{ns}	0.132
1-Octene	0.73^{ns}	nd	0.75^{ns}	0.089
(Z)-2-Octene	nd	nd	0.79	<0.001
Decane	nd	2.94^{ns}	2.53^{ns}	0.003
3-Ethyl-1,5-octadiene	nd	nd	4.82	<0.001
4,8-Dimethyl-1,7-nonadiene	nd	nd	4.26	<0.001
Ethylbenzene	1.39^b	2.98^a	nd	0.037
p-Xylene	2.14^b	2.80^b	4.62^a	<0.001
(E)-5-Octadecene	nd	2.56^b	9.43^a	<0.001
Styrene	1.43^{ns}	2.74^{ns}	1.36^{ns}	0.216
3-Cyclohexene-1-methanol *α-α*, 4-Trimethyl	8.44^a	8.50^a	6.32^b	0.039
α-α, Dimethyl benzyl alcohol	nd	2.49	nd	<0.001
1,2-Dimethoxy-4-(2-propenyl)benzene	2.59^b	4.90^a	2.18^b	<0.001
Methoxy-phenyl-oxime	nd	8.20	nd	<0.001

a-c, different letters indicate a significant difference at $p \leq 0.05$. Least squares means expressed as total area counts x 10^{-5}.

nd, not detected. ns, not significant.

The headspace composition of the examined pâtés also was characterized by the presence of high amounts of alcohols, above all ethanol, 1-butanol, 1-hexanol, (E)-3-hexen-1-ol, and (Z)-2-hexen-1-ol, as well as by aldehydes, such as hexanal and 2-hexenal (significantly higher in F4 and attributed to the presence of mushrooms and dried tomatoes).

The majority of alcohols are by-products of some pathways involving the aldehydes. Once formed, the aldehydes undergo a series of enzymatic transformations mediated by isomerases and alcohol dehydrogenases that generate C6 alcohols (CAVALLI *et al.*, 2004). C6 volatile alcohols are also important components of the flavour of fruits, vegetables, and leaves (SCHWAB *et al.*, 2008).

Regarding the most abundant alcohols, no significant differences were observed for ethanol in the three selected formulations, and for 1-butanol between F4 and F5 (attributable to the use of capers and salted anchovies, respectively). High levels of 1-hexanol were observed for F3 and F4 pâtés, as well as of (Z)-3-hexen-1-ol for F3 and F5, and (Z)-2-hexen-1-ol for F3. The presence of these volatiles is principally linked to the use of table olives and extra-virgin olive oil; a further contribution of 1-hexanol could be attributed to mushrooms and, above all, to dried tomatoes where it is considered one of the most important volatile compounds (CHRISTENSEN *et al.*, 2007). On the other hand, (Z)-3-hexen-1-ol could be related to arugula, whose headspace analysis showed this compound as the major contributor of aroma (data not shown). Significantly higher values of benzaldheyde were found in F4 more than in the other two formulations. This compound, present in all the examined raw materials, but at particularly high levels in roasted vegetables, is a powerful volatile having an aroma of bitter almond. It can be thermally generated from phenylalanine (CHU and YAYLAYAN, 2008) via the Strecker degradation.

The presence of salted anchovies in F5 could justify the significantly higher content of 2-methylbutanal, 3-methylbutanal, (E)-2-heptenal, (E,E)-2,4-heptadienal, and nonanal. The first two volatile compounds derived from catabolism of specific amino acids such as isoleucine and leucine, respectively, through the non-enzymatic Strecker reaction (ESTÉVEZ *et al.*, 2011) while the other volatile compounds were oxidation-derived compounds, dueto the effect of salting that caused a marked increase of these compounds with respect to fresh sample (SOLIMAN *et al.*, 1983). In particular, (E)-2-heptenal is associated to oxidized, tallow, pungent aroma; (E,E)-2,4-heptadienal to boiled-potato like odour (RUSTAD, 2009) and fatty, rancid aroma; nonanal to fatty, waxy, and pungent aroma.

The F5 pâté was also rich in esters, especially ethyl acetate, related to the presence of balsamic vinegar (DEL SIGNORE, 2001) and anchovies (HUMAID and JAMAL, 2014) among the ingredients. Moreover, the presence of dipropyl disulfide in F5 is due to the addition of onions to its formulation (CARSON, 1987).

Fig. 2 shows the results of quantitative descriptive sensory analysis and the results of two-way ANOVA, performed on the three selected formulations.

From the textural point of view, the three formulations did not show a phase separation, indicating a good homogenization and consequently an appropriate ratio among the ingredients. No significant differences were found among the tested formulations. The consistency (Fig. 3), instead, was significantly higher in F3 than F4 and F5, probably due to the different water content of the ingredients used. In terms of colour, all the examined samples showed generally low and high values for brightness and colour homogeneity, respectively.
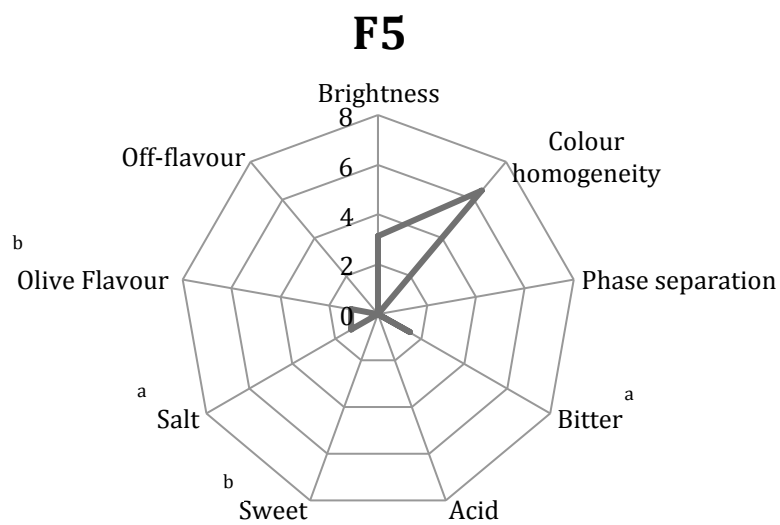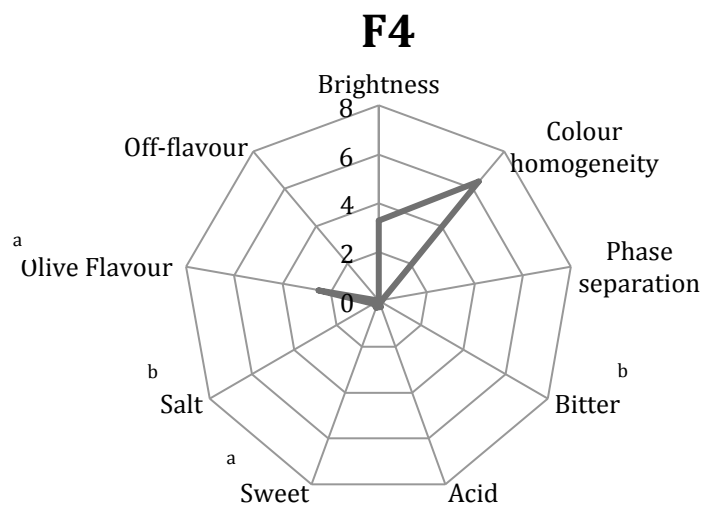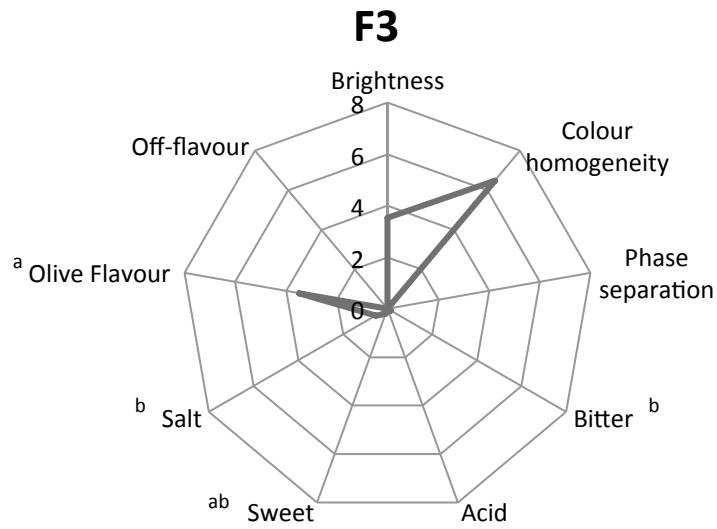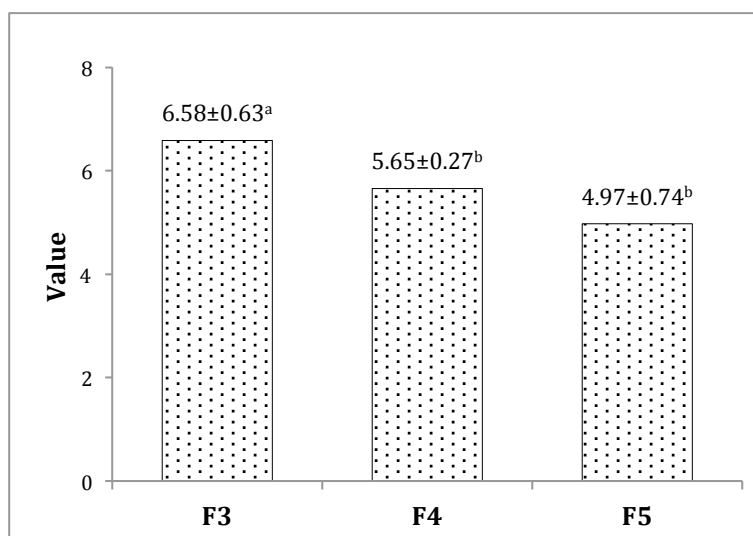
F3

F4

F5

Figure 2. Sensory profile of the three selected olive-based pâtés. a-b, different letters indicate a significant difference at $P \leq 0.05$ (Cosmai *et al*.).

About taste descriptors, the intensity of their perception was low, except in F5 for bitter - where was attributable to the use of onion and arugula - and for salty sensations, due to the use of salted anchovies. Moreover, the presence of anchovies could explain the significant lower olive flavour assessed in F5. No off-flavour was perceveid in the tested formulations.

Figure 3. Consistency values of the three selected olive-based pâtés. a-b, different letters indicate a significant difference at $P \leq 0.05$ (Cosmai *et al.*).

4. CONCLUSIONS

The obtained results showed a good overall acceptability of the examined pâtés. The ingredients used in the recipe allowed their clear differentiation and identification. The microbiological analyses ensured the safeness of the product. Moreover, the obtained results evidenced that it is possible to produce innovative formulations of olive-based pâtés by adding new ingredients to their recipes, and representing also a viable alternative use to unsuitable table olives not to be marketed as such.

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