Talanta 176 (2018) 610–618

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Perception of olive oils sensory defects using a potentiometric taste device

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ARTICLE INFO

Keywords:
Olive oil
Sensory analysis
Sensory defects
Potentiometric electronic tongue
Chemometrics

ABSTRACT

The capability of perceiving olive oils sensory defects and intensities plays a key role on olive oils quality grade classification since olive oils can only be classified as extra-virgin if no defect can be perceived by a human trained sensory panel. Otherwise, olive oils may be classified as virgin or lampante depending on the median intensity of the defect predominantly perceived and on the physicochemical levels. However, sensory analysis is time-consuming and requires an official sensory panel, which can only evaluate a low number of samples per day. In this work, the potential use of an electronic tongue as a taste sensor device to identify the defect predominantly perceived in olive oils was evaluated. The potentiometric profiles recorded showed that intra- and inter-day signal drifts could be neglected (i.e., relative standard deviations lower than 25%), being not statistically significant the effect of the analysis day on the overall recorded E-tongue sensor fingerprints (*P*-value = 0.5715, for multivariate analysis of variance using Pillai's trace test), which significantly differ according to the olive oils' sensory defect (*P*-value = 0.0084, for multivariate analysis of variance using Pillai's trace test). Thus, a linear discriminant model based on 19 potentiometric signal sensors, selected by the simulated annealing algorithm, could be established to correctly predict the olive oil main sensory defect (fusty, rancid, wet-wood or winey-vinegary) with average sensitivity of 75 ± 3% and specificity of 73 ± 4% (repeated K-fold cross-validation variant: 4 folds×10 repeats). Similarly, a linear discriminant model, based on 24 selected sensors, correctly classified 92 ± 3% of the olive oils as virgin or lampante, being an average specificity of 93 ± 3% achieved. The overall satisfactory predictive performances strengthen the feasibility of the developed taste sensor device as a complementary methodology for olive oils' defects analysis and subsequent quality grade classification. Furthermore, the capability of identifying the type of sensory defect of an olive oil may allow establishing helpful insights regarding bad practices of olives or olive oils production, harvesting, transport and storage.

1. Introduction

Olive oil is one of the oldest known vegetable oils produced in the Mediterranean countries. Olive oils may be graded according to its overall physicochemical composition and sensorial attributes as extra-virgin olive oils (EVOOs), virgin olive oils (VOOs) or lampante olive oils (LOOs). Since olive oils are a food product quite prone to frauds, protection legal regulations have been implemented by the European Union Commission [1–3], which take into account maximum levels of chemical and physicochemical parameters (e.g., free acidity, peroxide value, UV extinction coefficients, wax and alkyl esters contents) as well as sensory evaluation (presence/absence of organoleptic defects and the positive fruity sensation) [4–7].

Several analytical techniques have been described in the literature to detect and/or verify possible frauds involving the production and commercialization of olive oils, in order to guarantee consumer's

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http://dx.doi.org/10.1016/j.talanta.2017.08.066
Received 31 May 2017; Received in revised form 15 August 2017; Accepted 20 August 2017
Available online 31 August 2017
0039-9140/

confidence when purchasing this high-value product and to minimize the risk of unfair competition among olive oil producers. Official methods and recommended practices have been established by the American Oil Chemists' Society to assess olive oil quality [8]. However, some of these methods are quite expensive, non-green techniques, and require fulfillment of straight standardized procedures to ensure accuracy. On the other hand, the assessment of the positive and negative sensory attributes of olive oils is required for their quality grade classification being, at the present time, the evaluation by an official taste panel the only homologated method [1–3]. However, this official methodology has several drawbacks, namely experts' subjectivity, variability of responses over time, lack of reference standards and low number of analyses per day [9].

The development of an objective, rapid, automated, low-cost and precise methodology to assess sensory properties using instrumental techniques is envisaged as an alternative/complementary solution to taste panels. Several approaches have been proposed as alternatives to human sensory panels to evaluate the quality of olive oil (positive and/or negative attributes), namely those based on the individual or fused application of electronic noses, tongues and/or eyes (E-nose, E-tongue and/or E-eye), based on different analytical procedures and principles [5,6,10–13]. Qualitative and/or quantitative E-tongue based approaches have been successfully reported for olive oils physicochemical and positive sensory sensations assessment [10,13–21]. In which concerns the evaluation of negative sensory attributes, Borràs et al. [4] proposed partial least squares discriminant classification models, based on mid-infrared spectra, to differentiate EVOOs (defect absent) from lower quality olive oils (defect present). Recently, this same research team demonstrated the feasibility of fusing an E-nose (based on headspace mass spectrometry), an E-tongue (based on mid-infrared spectroscopy) and an E-eye (based on UV–Vis spectrophotometry) to discriminate EVOO, VOO and LOO, to detect the main off-flavors (fusty, musty, rancid and winey-vinegary) of olive oils and to predict the intensity scores of the main sensory attributes of olive oils evaluated by a human taste panel [5,6]. The capability of a potentiometric E-tongue with cross-sensitivity and non specific lipid polymeric membranes to correctly classify olive oils according to the sensory intensity perception levels (i.e., intense, medium and light) of positive attributes (fruity, bitter and pungency) has been shown by our research team [13]. A similar electrochemical device was also used to classify table olives according to the sensory quality category based on the intensity of the defect predominantly perceived (DPP), to differentiate organoleptic negative attributes that may be perceived in table olives, using standard solutions and real samples as well as to quantify the intensity of the DPP in table olive and respective brine solutions as well as to evaluate table olives' gustatory attributes (e.g., acid, bitter and salty sensations) [22–24]. Furthermore, this type of E-tongue device showed quantitative responses towards polar compounds (aldehydes, esters and alcohols) usually found in olive oils and that are related to their sensory positive attributes (e.g., green and fruity) [25]. The E-tongues successful performances may be attributed to the capacity of the lipid polymeric sensor membranes to promote interactions with polar taste substances via electrostatic or hydrophobic interactions, which are usually presented in the olive oils' alcoholic extracts [26,27]. In this work, the potential application of a potentiometric E-tongue, comprising lipid polymeric membranes, for olive oils' classification according to the sensory defect predominantly perceived (DPP) is evaluated as well as for classifying olive oils with sensory defects according to their quality grade. For this, a chemometric approach involving linear discriminant analysis (LDA) coupled with the simulated annealing (SA) variable selection algorithm, is applied and its predictive performance assessed based on two cross-validation variants: leave-one-out cross validation (LOO-CV) and repeated K-fold cross-validation (repeated K-fold-CV with 10 repeats and 4 folds).

2. Materials and methods

2.1. Olive oil samples, sensory and physicochemical analysis

Portuguese olive oils from different commercial brands were bought in supermarkets or obtained from local producers (Trás-os-Montes region, northeast of Portugal), being selected for this study 42 independent olive oils for which at least one organoleptic defect could be perceived by sensory panelists. Thus, according to EU Commission Regulations [1–3], no olive oil could be classified as EVOO. All olive oils were assessed by 8 trained panelists, following the methods and standards adopted by the International Olive Council (IOC) [28,29] for sensory analysis of olive oils, being in each sample perceived from one up to three simultaneous sensory defects of a total of four different negative organoleptic sensations: fusty, rancid, wet-wood and winey-vinegary defects. Each olive oil was coded according to the defect predominantly perceived (DPP) if more than one sensory defect was detected. Also, the median intensity of the DPP was assessed (DPP ≤ 3.5 or DPP > 3.5, for an intensity scale ranging from 0 (no defect perceived) to 10 (maximum intensity of defect perceived)). Furthermore, a physicochemical analysis was also carried out for the 42 olive oils under study at the laboratories of the School of Agriculture of the Polytechnic Institute of Bragança (Portugal). The physicochemical analysis followed the standard methods and the EU Commission Regulations [1–3], being quantified the values of five quality parameters, namely the free acidity (FA, in % oleic acid), the peroxide values (PV, in mEq O_2/kg) as well as the specific coefficients of extinction at 232 nm and 270 nm (K_{232}, K_{270} and ΔK). Additionally, the oxidative stability (OS, in hours) of each olive oil sample was also assessed based on Rancimat assays as previously described by Rodrigues et al. [19], which although not required for olive oil quality grade classification is an useful parameter for inferring about olive oil shelf life. All physicochemical assays were carried out in triplicate (i.e., 3 subsamples were collected from each olive oil bottle and analyzed). Based on the physicochemical mean contents and the sensory analysis and taking into account the guidelines of the European Regulations [1–3], each of the 42 olive oils were classified (Table 1) as VOO (simultaneously: FA ≤ 2.0% oleic acid, PV ≤ 20 mEq O_2/kg, K_{232} ≤ 2.60, K_{270} ≤ 0.25 and ΔK ≤ 0.01 and DPP ≤ 3.5) or LOO (for the other cases).

2.2. E-tongue device

The E-tongue (Fig. 1) included two home-made print-screen potentiometric arrays each one with 20 cross-sensitivity membranes as chemical sensors (diameter: 3.6 mm; thickness: 0.3 mm). As previously described by Dias et al. [30], a polyvinyl chloride (PVC) board was covered with a sticker (on both sides) with the printed scheme of the limits of the multi-sensor system (negative scheme), which was covered with a silver epoxy resin (EPO-TEK E4110) and dried overnight in an oven at 40 °C. After that, the sticker was removed, leaving the printed scheme (positive scheme) on the PVC board. Adhesives were placed at both ends of the board allowing protecting the board wells where the polymeric membranes will be placed as well as the RS-232 plug connection end. Then, the entire PVC board was covered with an acrylic resin (PLASTIK 70) for obtaining a waterproof surface, which required the application of multiple layers of the aerosol. After this step, the adhesives were removed and, in a first step, the RS-232 plug was placed, fixed with ARALDITE epoxy resin, where 20 pins were connected to the scheme of the PVC board using silver epoxy resin. In the second and last step, lipid polymeric membranes were prepared directly at each of the board wells according to the multi-sensor scheme, using the drop-by-drop technique. The volatile solutions used to prepare the lipid polymeric membranes were mixtures correspond-

Table 1
Olive oils physicochemical and sensory data and respective quality grade classification.

Olive oil (OO) sample code	Physicochemical analysis[a] Free acidity (% oleic acid)	Peroxide value (mEq O_2/kg)	K_{232}	K_{270}	ΔK	Oxidative stability (h)	Sensory analysis[b] Defect predominantly perceived: Type	Intensity	Other sensory defects	Olive oil quality grade[c]
OO1	0.38	11.6	1.548	0.089	−0.002	6.78	Fusty	≤ 3.5	n.d.	VOO
OO2	0.38	10.7	1.410	0.093	0.000	6.59	Fusty	≤ 3.5	n.d.	VOO
OO3	0.47	10.7	1.320	0.097	0.000	8.53	Rancid	> 3.5	Fusty	LOO
OO4	0.38	9.9	1.364	0.094	0.000	8.05	Rancid	> 3.5	Fusty	LOO
OO5	1.13	243.1	8.794	1.044	0.027	0.09	Rancid	> 3.5	n.d.	LOO
OO6	1.04	241.4	9.780	1.015	0.024	0.09	Rancid	> 3.5	n.d.	LOO
OO7	0.47	14.1	1.917	0.145	0.000	6.95	Rancid	> 3.5	Winey-vinegary	LOO
OO8	0.38	13.3	1.787	0.153	−0.001	6.54	Rancid	> 3.5	Winey-vinegary	LOO
OO9	0.38	17.4	2.201	0.118	−0.002	5.85	Winey-vinegary	> 3.5	Fusty, rancid	LOO
OO10	0.38	17.4	2.343	0.112	−0.001	5.44	Winey-vinegary	> 3.5	Fusty, rancid	LOO
OO11	0.47	19.9	1.922	0.149	−0.001	6.68	Wet-wood	> 3.5	Winey-vinegary	LOO
OO12	0.47	18.3	2.114	0.157	0.001	6.49	Wet-wood	> 3.5	Winey-vinegary	LOO
OO13	0.28	11.6	1.751	0.125	0.000	7.05	Winey-vinegary	≤ 3.5	n.d.	VOO
OO14	0.28	10.8	1.990	0.129	0.000	6.47	Winey-vinegary	≤ 3.5	n.d.	VOO
OO15	0.38	25.7	4.298	0.248	0.007	2.17	Rancid	> 3.5	n.d.	LOO
OO16	0.28	25.7	4.121	0.239	0.007	2.06	Rancid	> 3.5	n.d.	LOO
OO17	0.38	15.0	1.517	0.131	0.001	6.69	Rancid	≤ 3.5	Winey-vinegary	VOO
OO18	0.47	15.8	1.420	0.128	0.001	6.40	Rancid	≤ 3.5	Winey-vinegary	VOO
OO19	0.47	10.0	1.048	0.105	−0.001	7.39	Winey-vinegary	> 3.5	Rancid	LOO
OO20	0.38	10.0	1.241	0.125	0.000	7.52	Winey-vinegary	> 3.5	Rancid	LOO
OO21	0.47	10.8	1.370	0.105	0.000	7.24	Fusty	≤ 3.5	n.d.	VOO
OO22	0.47	10.0	1.300	0.100	0.000	7.54	Fusty	≤ 3.5	n.d.	VOO
OO23	0.38	9.1	1.167	0.167	0.004	10.46	Rancid	> 3.5	n.d.	LOO
OO24	0.47	9.1	1.327	0.178	0.003	10.09	Rancid	> 3.5	n.d.	LOO
OO25	0.38	10.0	2.064	0.156	0.001	6.71	Wet-wood	≤ 3.5	Rancid	VOO
OO26	0.38	10.8	2.177	0.154	0.000	6.65	Wet-wood	≤ 3.5	Rancid	VOO
OO27	0.38	20.0	2.346	0.171	0.002	3.62	Rancid	> 3.5	Fusty	LOO
OO28	0.47	18.3	2.509	0.156	0.002	3.49	Rancid	> 3.5	Fusty	LOO
OO29	0.28	8.3	2.150	0.119	0.000	7.41	Wet-wood	≤ 3.5	n.d.	VOO
OO30	0.38	7.5	2.084	0.131	−0.001	7.22	Wet-wood	≤ 3.5	n.d.	VOO
OO31	0.75	12.5	1.955	0.190	0.000	11.44	Winey-vinegary	> 3.5	n.d.	LOO
OO32	0.85	11.6	1.858	0.177	0.000	11.95	Winey-vinegary	> 3.5	n.d.	LOO
OO33	0.38	9.2	2.076	0.104	−0.001	4.28	Wet-wood	≤ 3.5	Winey-vinegary, Fusty	VOO
OO34	0.38	10.8	2.276	0.102	0.000	4.03	Wet-wood	≤ 3.5	Winey-vinegary, Fusty	VOO
OO35	0.47	13.2	2.191	0.153	−0.001	9.28	Wet-wood	≤ 3.5	n.d.	VOO
OO36	0.38	12.4	2.192	0.150	−0.001	9.19	Wet-wood	≤ 3.5	n.d.	VOO
OO37	0.47	12.5	2.040	0.151	0.000	5.60	Winey-vinegary	≤ 3.5	n.d.	VOO
OO38	0.57	10.8	2.076	0.136	0.001	5.23	Winey-vinegary	≤ 3.5	n.d.	VOO
OO39	0.47	7.5	1.626	0.102	0.000	6.74	Wet-wood	> 3.5	Winey-vinegary	LOO
OO40	0.47	7.5	1.622	0.200	0.005	6.74	Wet-wood	> 3.5	Winey-vinegary	LOO
OO41	0.75	14.1	2.520	0.198	0.005	4.37	Winey-vinegary	> 3.5	n.d.	LOO
OO42	0.66	14.9	2.955	0.185	0.006	3.93	Winey-vinegary	> 3.5	n.d.	LOO

[a] Physicochemical parameters evaluated according to the EU Commission Regulation [1–3].
[b] Sensory analysis was performed by trained panelists following the IOC regulations [28,29].
[c] Olive oil quality grade classification based on the physicochemical levels and the sensory analysis [1–3,28,29]: EVOO (simultaneously: FA ≤ 0.8% oleic acid, PV ≤ 20 mEq O_2/kg, K_{232} ≤ 2.50, K_{270} ≤ 0.22, ΔK ≤ 0.01 and DPP = 0); VOO (simultaneously: FA ≤ 2.0% oleic acid, PV ≤ 20 mEq O_2/kg, K_{232} ≤ 2.60, K_{270} ≤ 0.25, ΔK ≤ 0.01 and 0 < DPP ≤ 3.5) or LOO (for the other cases).

ing to different combinations of 4 different lipid additives (octadecylamine, oleyl alcohol, methyltrioctylammonium chloride and oleic acid; ≈3%); 5 different plasticizers (bis(1-butylpentyl) adipate, dibutyl sebacate, 2-nitrophenyl-octylether, tris(2-ethylhexyl)phosphate and dioctyl phenylphosphonate; ≈ 65%) and high molecular weight polyvinyl chloride (PVC; ≈ 32%). All reagents were from Fluka (minimum purity ≥ 97%). Although the two arrays comprised sensors with the same combinations of lipid additive/plasticizers/PVC and with the same relative composition, they could present different electrochemical properties since the manual drop-by-drop technique used may allow

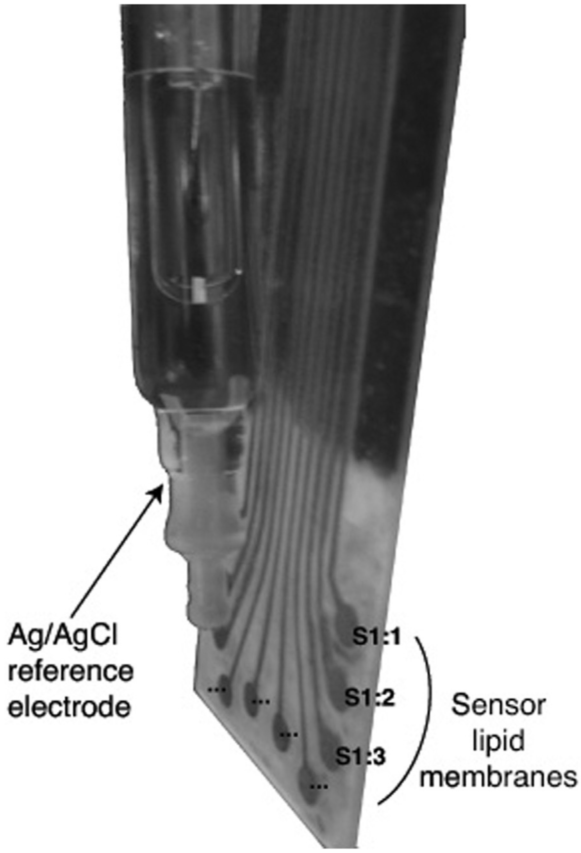

Fig. 1. Potentiometric E-tongue device.

Table 2
E-tongue sensors details (identification code; pairs of plasticizer additive compounds, used in the preparation of each lipid-polymeric membrane).

Sensor code		Plasticizer (~65%)	Additive (~3%)
1st array	2nd array		
S1:1	S2:1	2-Nitrophenyl-octyl ether	Octadecylamine
S1:2	S2:2		Oleyl alcohol
S1:3	S2:3		Methyltrioctylammonium chloride
S1:4	S2:4		Oleic acid
S1:5	S2:5	Tris(2-ethyl-hexyl) phosphate	Octadecylamine
S1:6	S2:6		Oleyl alcohol
S1:7	S2:7		Methyltrioctylammonium chloride
S1:8	S2:8		Oleic acid
S1:9	S2:9	Dibutyl sebacate	Octadecylamine
S1:10	S2:10		Oleyl alcohol
S1:11	S2:11		Methyltrioctylammonium chloride
S1:12	S2:12		Oleic acid
S1:13	S2:13	Bis(1-butylpentyl) adipate	Octadecylamine
S1:14	S2:14		Oleyl alcohol
S1:15	S2:15		Methyltrioctylammonium chloride
S1:16	S2:16		Oleic acid
S1:17	S2:17	Bis(2-ethylhexyl) phthalate	Octadecylamine
S1:18	S2:18		Methyltrioctylammonium chloride
S1:19	S2:19		Oleyl alcohol
S1:20	S2:20		Oleic acid

obtaining inhomogeneous membranes with different physical properties (e.g., different membrane transparency levels and porosity leading to different adsorption phenomena and surface chemical reactions, which may lead to deviations in sensors' readings). Therefore, instead of assuming a set of 20 sensor-sensor replica membranes it is more realistic to consider the use of 40 independent sensors. The multi-sensor system was used together with an Ag/AgCl reference electrode (Crison, 5241), forming a multi-sensor device that allowed the potentiometric measurements with a multiplexer Agilent Data Acquisition Switch Unit model 34970A, controlled with the Agilent BenchLink Data Logger software installed on a PC. The multi-sensor device was placed in a KCl aqueous solution (1 mol/L) until used for analysis. To keep the uniformity with previous works, each sensor was identified with a code that includes a letter S (for sensor) followed by the number of the array (1 or 2) and the number of the membrane (1–20, corresponding to different combinations of plasticizer and additive used) as described in Table 2.

2.3. E-tongue analysis: olive oils sample preparation and potentiometric assays

All samples were electrochemically analyzed in the same day avoiding the need of statistical complex signal pre-treatments to overcome possible signal drifts issues. Indeed, it has been reported that potentiometric signals gathered by lipid polymeric membranes (similar to those comprised in the E-tongue device used in this work) during the analysis (three times in day, corresponding to a 5 h interval) of aqueous standard solutions of basic tastes (acid, bitter and salty) had satisfactory intra-day repeatabilities (relative standard deviation percentages, RSD% varying from 0.1% to 12%) [24]. The low RSD% values reported for usual time analysis periods (5 h), strengthen the satisfactory E-tongue signals stability in time. On the other hand, based on the experience of the research team, which used the same E-tongue device in several works, this type of potentiometric E-tongue could be used during at least one year period without requiring any replacement of the lipid polymeric sensor membranes, showing the storage stability of this type of sensor device. Furthermore, in previous works of the research team, it was verified that the lipid polymeric sensor membranes showed quantitative linear (sensitivities, mV/decade) response towards the decimal logarithm of the concentration of chemical standard solutions mimicking positive or negative sensory attributes usually perceived in olives or olive oils [22,24,25]. It should be emphasized that the sensing mechanism depends on the non-uniform hydrophilicity of the lipid membranes and on the ionic environment at the proximity of the membrane surface. Thus, the measured electric potential depends on the membrane surface-charge density changes, which are dependent of the surface electric charge density and of its permeability to ions altered by the physical adsorption of non-electrolytes compounds [31–33]. Nevertheless, if the electrochemical analysis required several days, possible signal drifts could be solved by signal pre-treatment techniques such as subtracting the average signal profile recorded by the E-tongue device during the analysis of each olive oil sample by the average signal profile recorded for a specific standard solution [19]. In this context, and to discard the need of signal pre-treatment due to the occurrence of drift issues, in the present work, intra-day and inter-day sensor signal repeatabilities were evaluated by calculating the RSD% related to the analysis of different olive oils (independent samples) for which a single sensory defect was perceived by the panelists (number of independent defected olive oils × 2 extractions × 2 assays) in the same day or in two consecutive days. This evaluation would allow verifying the occurrence of signal drifts and the need of signal pre-treatment. The olive oil extraction procedure used was previously described by Dias et al. [26]. Hydro-ethanolic solutions (H_2O:EtOH, 80:20 v/v) were used to overcome the difficulty of carrying out electrochemical assays in viscous non-conductive liquids [10]. Ethanol was of analytical grade (Panreac, Barcelona) and deionized water type II was used. For the electrochemical assays, samples were withdrawn from each olive oil bottle after a smooth shaken, and extracted. In each assay, 10.00 g of olive oil were mixed to 100 mL of hydro-ethanolic solution during 5–10 min under strong agitation, using a vortex stirrer (LBX V05 series, lbx instruments), with a constant speed of approximately 500 rpm. This process allowed the extraction of polar compounds, which are responsible for sensory attributes of olive oils [10,13,25,26]. The mixture was left at ambient temperature during 60 min, after which, 40.0 mL of the supernatant solution was carefully removed and immediately analyzed with the E-tongue. The electrochemical analysis took 5 min enabling to carried out several electrochemical scans, being retained the last one, which would correspond to a pseudo-equilibrium state. Electrochemical assays were performed in duplicate for each sample unless the coefficients of variation of the potentiometric signals recorded by each E-tongue sensor were greater than 20% (value set according to the IOC regulations [28,29] for sensory analysis), in which cases a third assay was performed. As proposed by Rodrigues et al. [19], to minimize the risk of overoptimistic performance of the multivariate models, for data split (establishment of training and internal-validation sets) and modeling purposes, only one electrochemical "average" signal profile per sample was used, avoiding that results from duplicate assays of the same olive oil sample could be included into both training and validation sets.

2.4. Statistical analysis

A two-way multivariate analysis of variance (2-way MANOVA) was applied to evaluate the possible effects of the analysis day and/or type of sensory defect perceived in the olive oils, considering simultaneously all the dependent variables (i.e., E-tongue sensors signal profiles), using the Pillai's trace test, aiming to verify the statistical significance of the possible signals drifts as well as of the taste perception capability of the E-tongue device. The potential use of the olive oils' potentiometric E-tongue fingerprints for classifying olive oils according to the sensory defect predominantly perceived by trained panelists (i.e., fusty, rancid, wet-wood and winey-vinegary defects), regardless the olive oil quality grade, was further evaluated using the linear discriminant analysis (LDA), a supervised multivariate statistical technique, coupled with a meta-heuristic simulated annealing (SA) algorithm, which is a variable selection technique. The same electrochemical-chemometric approach was also applied to verify the capability of extracting valuable and representative information, contained on the potentiometric signals profiles recorded by the E-tongue device during the analysis of the hydro-ethanolic olive oils extracts, to classify olive oils according to their quality grade (VOO or LOO), independently of the type and number of organoleptic defects simultaneously perceived by the trained panelists. In this study, the most informative subsets of independent predictors (i.e., sensors) to be included in the final LDA models were chosen by applying a variable selection algorithm, since not all sensors present relevant information and so, their inclusion in the classification models may increase the noise effects. The best subsets of sensors (varying from 2 to 39) were established among the 40 potentiometric sensor signals using the SA variable selection algorithm [34–36]. The LDA potential was evaluated using two cross-validation (CV) variants: leave-one-out (LOO-CV), known to be an over-optimistic procedure; and, repeated K-fold (repeated K-fold-CV) technique. For the latter, data was randomly split into K folds, being each of the folds left out in turn and the other K-1 folds used to train the model. The held out fold was used for test purposes and the quality of the predictions was assessed using the average values of sensitivities (percentage of correct/true classifications) and specificities (assumed as the true negative rates). The K estimates are averaged to get the overall resampled estimate [36]. In this work the K-folds were set equal to 4, enabling the random formation of internal validation subsets (for each gustatory group) with 25% of the initial data, allowing bias reduction. The procedure was repeated 10 times for putting the model under stress. The repeated K-fold-CV technique allows reducing the uncertainty of the estimates, by evaluating the predictive performance of the models established using 4×10 random sub-sets for internal validation (i.e., 40 total resamples). To normalize the weight of each variable in the final linear classification model, variable scaling and centering procedures were evaluated. The classification performance of each LDA model was graphically evaluated using 2-D plot of the main discriminant functions (when more than two class groups were considered) or by plotting the 1-D frequency distribution of the data for the sole discriminant function, for the cases where only two classes were evaluated. For the multi-classes case, posterior probabilities were computed using the Bayes' theorem (which enables controlling over-fitting issues) to deeper assess the classification capability of the established LDA models (i.e., to infer the probability obtained after an event has been observed), being also plotted as the class membership boundary lines in the 2-D plots [37]. All statistical analysis were performed using the Subselect [35,38] and MASS [39] packages of the open source statistical program R (version 2.15.1), at a 5% significance level.

3. Results and discussion

3.1. Olive oils quality grade classification based on the physicochemical and sensory analysis

All the 42 olive oils studied in this work were analyzed taking into account the five physicochemical quality parameters required (FA, PV, K_{232}, K_{270} and ΔK) by the EU Commission Regulations [1–3] for quality grade classification of olive oils as EVOO, VOO or LOO, being also determined the OS values (Table 1). Based on the physicochemical levels determined it could be concluded that only 9 olive oils (sample codes: OO5, OO6, OO15, OO16, OO27, OO28, OO32, OO41 and OO42; FA > 0.8% oleic acid, PV > 20 mEq O_2/Kg, K_{232} > 2.5, K_{270} > 0.25 and/or ΔK > 0.01) would be graded as LOO, being all the other olive oils classified as EVOO (simultaneously: FA ≤ 0.8% oleic acid, PV ≤ 20 mEq O_2/kg, K_{232} ≤ 2.50, K_{270} ≤ 0.22 and ΔK ≤ 0.01). However, the results from the sensory analysis allowed perceiving at least one organoleptic defect in all the 42 commercial olive oils evaluated in this study, being possible to detect up to 3 different sensory defects in some olive oils (Table 1). So, regarding the quality grade, none of the olive oils studied could be classified as EVOO, being 18 classified as VOO and the other 24 as LOO, taking into account simultaneously the determined levels of the physicochemical parameters (FA, PV, K_{232}, K_{270} and ΔK) and the intensity of the DPP and the limit levels established by the EU Commission Regulations [1–3]. These findings show the importance of performing a sensory analysis to confirm the label correctness concerning olive oils' quality grade. The practical limitations related with sensory panels (i.e., availability, subjectivity, analysis cost, analysis time and low number of samples evaluated per day) strengthen the real need of establishing fast and accurate artificial sensory classifiers like that envisaged in the present study. Moreover, by identifying the organoleptic defect of an olive oil, valuable insights may be withdrawn concerning possible bad practices of olives or olive oils production, harvesting, transport and storage. The wet-wood defect may be related to bad practices at the olive production level, being fusty and winey-vinegary defects mainly related to bad practices of olives harvesting, transport and storage. On the other hand, rancid negative attribute may be partially due to bad olive oil storage conditions. In addition, it should be remarked that, with the exception of some olive oils, the interval range of the OS values (Table 1) are similar for VOO and LOO, which could be explained by the fact that this classification was mainly due to the sensory perception of defects and not to the olive oils physicochemical contents. Finally, based on the type of DPP, each olive oil was classified into one of the following groups: winey-vinegary olive oil (12 olive oils), wet-wood olive oil (12 olive oils), rancid olive oil (14 olive oils) and fusty/musty olive oil (4 olive oils).

3.2. Olive oils potentiometric signal profiles

Different potentiometric signal profiles (varying from −50 mV to +275 mV) were acquired by the 40 E-tongue sensors during the electrochemical analysis of the olive oils' hydro-ethanolic extracts. These differences were due to sensory defect predominantly perceived by the trained panelists (i.e., fusty, rancid, wet-wood and winey-vinegary as shown in Table 1) or to the olive oils quality grade, assessed according to the physicochemical and sensory data (i.e., VOO or LOO, since the perception of an organoleptic negative attribute does not allow classifying any olive oils as EVOO).

The potentiometric average signals recorded by each sensor for each of the four sensory defects perceived showed slight trend differences (magnitude of the potentiometric signal and/or dynamic signal range). These differences may allow the discrimination of the olive oils according to the sensory defect predominantly perceived (regardless the presence of other defects or the olive oil quality classification) or according to the quality grade of the olive oil (independently of the number and type of organoleptic defects simultaneously perceived).

On the other hand, the signal stability (or possible signal drift, commonly reported for potentiometric sensors) was evaluated using the relative standard deviations (RSD%) calculated based on the different electrochemical assays carried out in the same day (intra-day repeatability) or in two consecutive days (inter-day repeatability). For this study, only olive oils containing one of the four perceived sensory defects were used (i.e., fusty: 4 olive oils × 2 extractions × 2 assays, samples OO1, OO2, OO21 and OO22; rancid; 6 olive oils × 2 extractions × 2 assays samples OO5, OO6, OO15, OO16, OO23 and OO24; wet-wood: 4 olive oils × 2 extractions × 2 assays, samples OO29, OO30, OO35 and OO36; or, winey-vinegary: 8 olive oils × 2 extractions × 2 assays, samples OO13, OO14, OO31, OO32, OO37, OO38, OO41 and OO42; information gathered in Table 1). Nevertheless, this selection ensured an intrinsic variability due to the different olive oils analyzed, the extraction procedure and/or the duplicate electrochemical assays, for each main defect. The results showed that satisfactory RSD% values could be obtained, varying in general between 0.5% and 20% or 3.5% and 25% for the intra- or inter-day analysis, which are in agreement with those previously reported for intra-day repeatabilities of standard solutions mimicking acid, bitter and salty taste sensations (0.1% ≤ RSD% ≤ 12%) [24]. Fig. 2 shows, as an example, the average signal profiles recorded by the 1st sensor array of the E-tongue device (sensors: S1:1 to S1:20) during two consecutive days, for different olive oils (from 4 to 8 olive oils, depending on the sensory defect, each one extracted twice and electrochemically analyzed in duplicate) with a single perceived sensory defect (i.e., fusty, rancid, wet-wood or winey-vinegary). The overall satisfactory intra- and inter-day signal stability of the E-tongue pointed out that the potentiometric signal drift could be neglected, being patent the potentiometric signal stability over the two consecutive analysis days from the plots of Fig. 2. Furthermore, there is no clear day-dependence trend of the potentiometric signals recorded (considering the results from the two days of analysis), being signals increase or decrease dependent on the sensor and on the type of sensory defected olive oil. Also, the referred plots allow verifying that different potentiometric fingerprints could be obtained for olive oils with different sensory defects, being expectable that the recorded signal profiles could be used to discriminate olive oils according to the main sensory defect. Finally, the 2-way MANOVA results (Pillai's trace test) confirmed the previous conclusions, i.e., the analysis day does not have a significant statistical effect at a 5% significance level (P-value = 0.5715) when the all the signal potentiometric profiles are considered simultaneously but, on the other hand, the overall sensors' signal fingerprints significantly differ with the type of sensory defect perceived on the olive oils (P-value = 0.0084).

3.3. Discrimination of olive oils with sensory defects based on electrochemical profiles

The potentiometric signal data collected allowed to establish an E-tongue-LDA-SA model (3 discriminant functions explaining 93.5%, 3.6% and 2.9% of the original data variability) based on the signal profiles recorded with 19 E-tongue sensors (1st array sensors: S1:4, S1:5, S1:8, S1:12, S1:15, S1:16, S1:19 and S1:20; 2nd array sensors; S2:1, S2:8, S2:9, S2:11, S2:14, S2:15, S2:17, S2:18, S2:19 and S2:20), during the analysis of olive oils' hydro-ethanolic extracts. The proposed model enabled the correct classification of 98% for the original grouped data (Fig. 3) and 81% for the LOO-CV procedure, based on the potentiometric data. In fact, for the original data, the sensitivities varied from 92% for the winey-vinegary of defected olive oils to 100% for the fusty, rancid or wet-wood groups. An overall specificity of 99% was achieved with single specificities ranging from 96% for the rancid group to 100% for fusty, wet-wood or winey-vinegary groups. For the LOO-CV procedure, sensitivities of 75%, 64%, 83% and 100% and specificities of 95%, 89%, 100% and 90% were obtained for the classification of defected olive oils classified as fusty, rancid, wet-wood or winey-vinegary, respectively. These results showed that all samples classified as wet-wood defected olive oils were correctly classified and misclassification of other samples as having this specific defect did not occurred. Globally, the overall results pointed out that a mean specificity of 94% could be expected and that more than 89% of the correct classifications were not false predictions (true negative) for all groups evaluated. It should also be remarked that the majority of the misclassifications occurred between olive oils classified with winey-vinegary defect and rancid defect, which could be justified by the fact that in some of the commercial olive oils analyzed, more than one organoleptic defect could be perceived simultaneously by the panelists, turning out the E-tongue discrimination task more complex and challenging. The E-tongue-LDA-SA predictive performance was further verified using the repeated K-fold-CV procedure (4 folds and 10 repetitions, leading to 40 internal cross-validation test sets each composed by 10–11 samples composed by 1, 3–4, 3 and 3 samples of fusty, rancid, wet-wood and winey-vinegary groups, respectively). The results showed that the best predictive E-tongue-LDA-SA model based on the same 19 signal sensor profiles allowed achieving mean correct classification rates of 75 ± 3% (varying from 69% to 79% for each of the 10 random repetitions of the 4 folds data split) and an average specificity of 73 ± 4% (ranging from 67% to 80% for each of the 10 random repetitions of the 4 folds data split). The results obtained with this more realistic CV variant showed a similar effectiveness regarding the correct classification rates (sensitivities: 71 ± 16%, 60 ± 8%, 92 ± 6% and 77 ± 7%; and, specificities: 51 ± 13%, 71 ± 8%, 98 ± 4% and 70 ± 8%; for fusty, rancid, wet-wood and winey-vinegary defected olive oils, respectively) pointing out the consistency and robustness of the electrochemical analytical device as a practical classification tool of commercial sensory defected olive oils according to the main sensory defect perceived. In fact, the E-tongue-LDA-SA model selected allowed the correct classification of a defected olive oil sample according to its main sensory defect with average largest posterior probability of 0.97 ± 0.09 for fusty, 0.95 ± 0.11 for rancid, 0.99 ± 0.05 for wet-wood and 0.96 ± 0.10 for winey-vinegary negative attributes. Furthermore, for the majority of misclassification samples, the correct group had in general the second highest posterior probability. Finally, it is important to emphasize that these preliminary results are quite satisfactory taking into account the heterogeneity of the 42 commercial olive oils studied in this work (different brands, different olive cultivars, etc.), plus the fact that the olive oil samples evaluated had a high sensory complexity, being more than one sensory defect usually perceived simultaneously by the panelists.

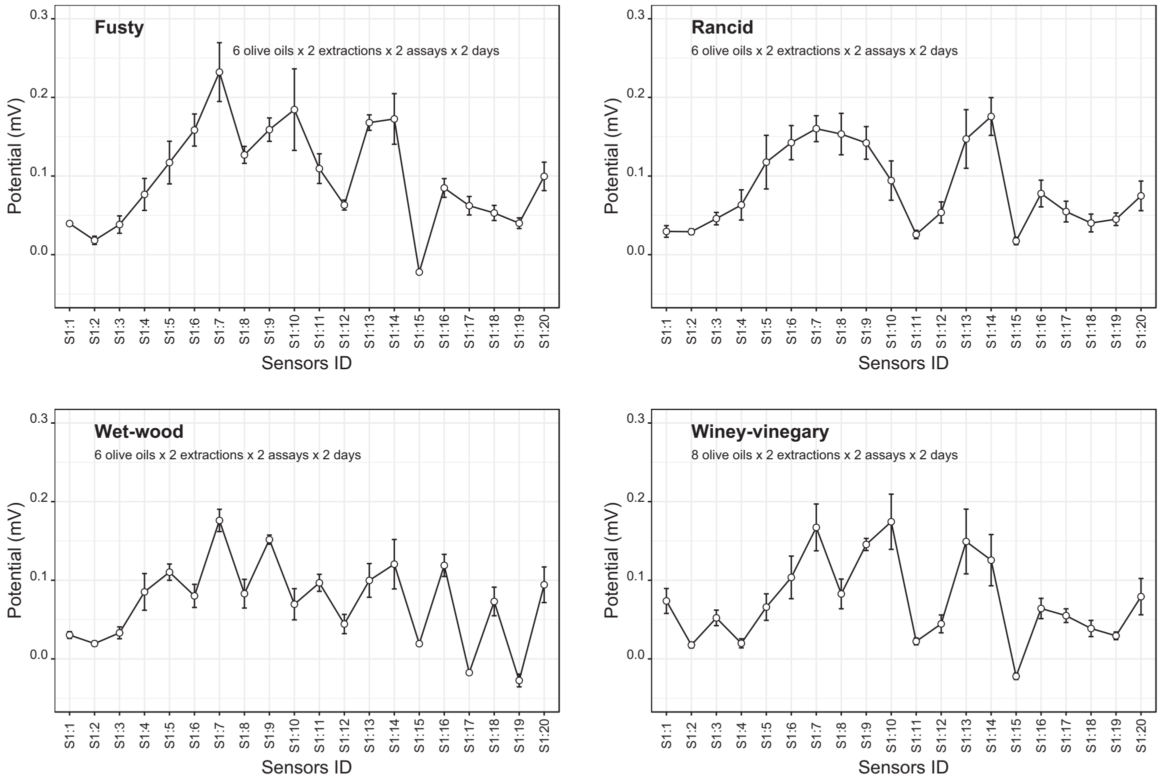

Fig. 2. Potentiometric mean signal profiles (error bars - related standard deviations) recorded by the 1st sensor array of the E-tongue device, concerning assays carried out in two consecutive days, of olive oils' hydro-ethanolic extracts of selected different olive oils for which a single sensory defect was perceived (i.e., fusty, rancid, wet-wood or winey-vinegary) by trained panelists.

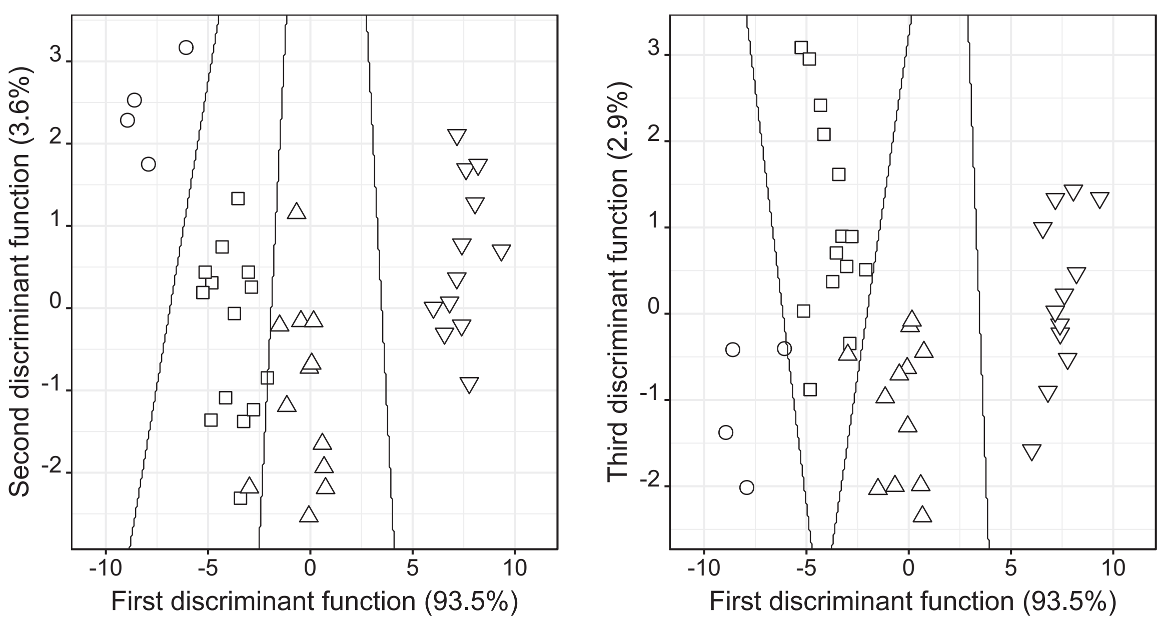

Fig. 3. Discrimination of commercial olive oils according to the defect predominantly (fusty, rancid, wet-wood or winey-vinegary) perceived by trained sensory panelists: plots of the three discriminant functions of the E-tongue-LDA-SA model based on the information of 19 signal sensor potentiometric profiles recorded during the olive oils hydro-ethanolic extracts analysis (1st array sensors: S1:4, S1:5, S1:8, S1:12, S1:15, S1:16, S1:19 and S1:20; 2nd array sensors; S2:1, S2:8, S2:9, S2:11, S2:14, S2:15, S2:17, S2:18, S2:19 and S2:20). The full lines represent the boundary lines based on the posterior probabilities calculated for each class membership.

3.4. Olive oils physicochemical quality discrimination based on electrochemical profiles

The potentiometric signal data collected also allowed to establish an E-tongue-LDA-SA model (with only one discriminant function that explained 100% of the original data variability) based on the signal profiles of 24 E-tongue sensors (1st array sensors: S1:2 to S1:8, S1:12, S1:14, S1:15, S1:19 and S1:20; 2nd array sensors; S2:1 to S2:5, S2:7, S2:10, S2:13, S2:16, S2:17, S2:18 and S2:20) to classify the olive oils as VOO or LOO. The proposed model enabled the overall correct

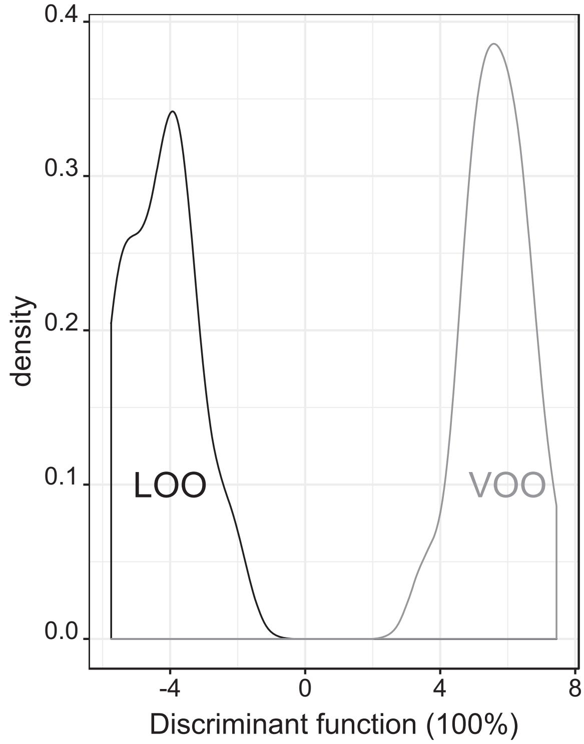

Fig. 4. Density distribution plot for olive oils quality grade classification (VOO and LOO) based on the discriminant function of the E-tongue-LDA-SA classification model based on 24 signal sensor potentiometric profiles recorded during the olive oils hydro-ethanolic extracts analysis (1st array sensors: S1:2 to S1:8, S1:12, S1:14, S1:15, S1:19 and S1:20; 2nd array sensors; S2:1 to S2:5, S2:7, S2:10, S2:13, S2:16, S2:17, S2:18 and S2:20).

classification of 100% for the original grouped data (corresponding to sensitivity and specificity values of 100%; Fig. 4). Also, for the LOO-CV procedure, an overall sensitivity of 98% and sensitivity of 97% were achieved, which were due to a LOO sample that was misclassified as VOO. It should be noticed that several of the sensors included in this quality grade classification model were also used in the E-tongue-LDA-SA classification model previously established for olive oils' defects discrimination. Similarly, for the repeated K-fold-CV variant (4 folds and 10 repetitions), the proposed E-tongue-LDA-SA model (based on the potentiometric profiles of the same 24 sensors) allowed an average correct class prediction (based on the sensitivity values for VOO and LOO groups) of 92 ± 3% (varying from 88% to 98% for each of the 10 random repetitions of the 4 folds data split) and an average specificity of 93 ± 3% (also ranging from 88% to 98% for each of the 10 random repetitions of the 4 folds data split), regardless the number of sensory defects simultaneously perceived in each sample. Concerning the olive oils classification according to the quality grade group, mean sensitivities of 94 ± 5% and 91 ± 6% were obtained for VOO and LOO samples, with mean specificities of 90 ± 7% and 95 ± 3%, respectively. Furthermore, it should be remarked that olive oils correctly classified according to their quality grade also showed largest average posterior probabilities, namely of 1.00 ± 0.01 and 1.00 ± 0.04 for VOO and LOO samples, respectively.

4. Conclusions

In this work, it was demonstrated the feasibility of applying a potentiometric E-tongue (with lipid cross-sensitivity polymeric membranes) in combination with chemometric tools, for the successful discrimination of olive oils with negative organoleptic attributes, which assessment is usually carried out by official trained sensory panels, turning out in an expensive and time-consuming task. In addition, the capability of identifying a specific sensory defect present in an olive oil is also relevant since it could give some important insights regarding possible bad practices at the olive production level (e.g., wet-wood), at the olives harvesting, transport and storage levels (e.g., fusty and winey-vinegary) or at the olive oil storage level (e.g., rancid). As well, it has been verified the versatility of this simple, low-cost and fast electrochemical tool to assess the quality grade of olive oils with organoleptic defects (VOO or LOO). Thus, this preliminary study shows the practical potential of this type of electrochemical tool (E-tongue) as a taste sensor device for the successful evaluation of organoleptic defects perceived in olive oils, which must be taken into account for their quality commercial grade classification.

Compliance with ethics requirements

Conflict of interest

Ana C.A. Veloso declares that she has no conflict of interest. Lucas M. Silva declares that he has no conflict of interest. Nuno Rodrigues declares that he has no conflict of interest. Ligia P.G. Rebello declares that she has no conflict of interest. Luís G. Dias declares that he has no conflict of interest. José A. Pereira declares that he has no conflict of interest. António M. Peres declares that he has no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent

Not applicable.

Acknowledgments

This work was financially supported by Project POCI-01–0145-FEDER-006984 – Associate Laboratory LSRE-LCM, Project UID/QUI/00616/2013 – CQ-VR, and UID/AGR/00690/2013 – CIMO all funded by FEDER - Fundo Europeu de Desenvolvimento Regional through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia, Portugal. Strategic funding of UID/BIO/04469/2013 unit is also acknowledged. Nuno Rodrigues thanks FCT, POPH-QREN and FSE for the Ph.D. Grant (SFRH/BD/104038/2014).

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