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Varietal discrimination of extra virgin olive oils by near and mid infrared spectroscopy

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ABSTRACT

The use of near and mid infrared spectroscopy, combined with chemometric analysis, was explored as a tool to classify samples of Italian extra virgin olive oil on the basis of the cultivar.
A total of 82 monovarietal samples ('Casaliva', 'Leccino' and 'Frantoio') of extra virgin olive oils were analysed. Several variables were measured: the free acidity, the peroxide value, spectrophotometric indices, the fatty acid composition, carotenoids, chlorophylls and tocopherol content. The same samples were also scanned by using NIR and MIR spectroscopy. The classification methods (LDA and SIMCA) were applied on chemical data and on the spectral data after having used the algorithm SELECT, as feature selection technique. The results showed that NIR and MIR spectroscopy is an interesting technique compared with traditional chemical index in classifying olive oil samples on the basis of the varietal origin.
The spectroscopic methods could represent a reliable, cheap and fast classification tool, not requiring chemical analyses for discrimination among cultivars.

1. Introduction

The extra virgin olive oil, owing to its high nutritional value and significant health benefits, is one of the most valuable ingredients of the Mediterranean diet.

Extra virgin olive oil composition determines its intrinsic quality and could be influenced by several factors. Cultivar, environment and horticultural techniques affect the fruit physiology (Tura et al., 2007). Other factors as latitude, climatic conditions, irrigation regime, fruit ripening, harvesting and extraction technologies influence the distributions of the fatty acids (D'Imperio, Dugo, Alfa, Mannina, & Segre, 2007; Stefanoudaki, Kotsifaki, & Koutsaftakis, 1999; Torres & Maestri, 2006) and triglycerides (Stefanoudaki, Kotsifaki, & Koutsaftakis, 1997).

The effect of cultivar and of its interaction with the environment on the qualitative profile and the oxidative stability of extra virgin olive oil have been studied by determining the concentration profiles of saturated and unsaturated fatty acids, triglycerides, diacylglycerols and triacylglycerols, sterols, phenolic compounds, hydrocarbons, pigments and volatile components. These compounds differ according to the fruit variety (Lerma-Garcıá, Herrero-Martínez, Ramis-Ramos, & Simó-Alfonso, 2008).

Traditionally, these parameters have been estimated by classical analytical methods, most of which are based on gas chromatography (GC) and high-performance liquid chromatography (HPLC). In the last few years, attention has been focused on authentication for genetic varieties of olive oils using nuclear magnetic resonance (NMR) fingerprinting (Camin et al., 2010; Mannina, Patumi, Proietti, Bassi, & Segre, 2001).

Nevertheless, all these methods have several drawbacks, the most significant of which are low speed, high cost, and the necessity of sample pre-treatments and of highly-skilled personnel.

Infrared spectroscopy in both the near (NIR) and mid (MIR) regions, combined with multivariate data analysis, has proven to be a successful analytical method for quantitative and qualitative modelling of a wide variety of food and food process. These techniques facilitate real-time measurements at all stages of production, and they offer a fast, non-destructive and cost effective method of food analysis (Fagan & O'Donnell, 2008; Woodcock, Downey, & O'Donnell, 2008).

Recent applications of NIR and MIR spectroscopy in edible oil analysis, reported in literature, include quality parameter determination (Ahmed, Daun, & Prybylski, 2005; Azizian & Kramer, 2005) and adulteration detection (Banu & Mauer, 2002; Maggio, Cerretani, Chiavaro, Kaufman, & Bendini, 2010). These methods have been successfully applied in authentication studies of olive oil on the basis of geographical origin (Bendini et al., 2007; Casale, Casolino, Ferrari, & Forina, 2008; Galtier et al., 2008; Sinelli, Casiraghi, Tura, & Downey, 2008), but there is not any study regarding the application of these

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molecular vibration spectroscopy in varietal discrimination of extra virgin olive oils.

The objective of this paper has been to investigate the potential of NIR and MIR spectroscopy, combined with chemometric data analysis, to classify three monovarietal Italian extra virgin olive oils (Casaliva, Leccino, and Frantoio) on the basis of varietal origin. In conjunction with this, traditional chemical indices were evaluated in order to verify the feasibility of NIR and MIR as a rapid non-invasive method for classifying extra virgin olive oils of different cultivars.

2. Experimental

2.1. Oil sampling

A total of 82 monovarietal extra virgin olive oils were analysed. This sample set comprised oils obtained by three single-cultivars: 'Casaliva', 'Leccino' and 'Frantoio' (27 from Casaliva, 28 from Leccino and 27 from Frantoio). Each cultivar was grown in three different orchards (Puegnago, Follonica and Mirto) representative of Italian olive growing regions. In particular, Puegnago is representative of the Garda Bresciano area (western shore of Lake Garda) in Lombardy region (northern Italy); Follonica of the Tyrrhenian cost area in Tuscany region (central Italy) and Mirto of the Ionian cost area in the Calabria region (southern Italy).

The monovarietal extra virgin olive oil samples were obtained from 6 to 10 kg of olives using a standard continuous procedure in a mini oil mill (Toscana Enologica Mori, mod. Mini 50 modified — Tavarnelle Val Di Pesa) within three days of picking. The olives, collected at commercial maturity, were crushed with a hammer mill and the crushed olive paste was then submitted to a malaxation (20 °C for 30 min) to allow the microscopic oil droplets to coalesce into larger globules. The oil was extracted by hydraulic press (maximum 20 MPa) and separated by centrifugation for 10 min at 3000 rpm.

2.2. Methods

2.2.1. Chemical analyses

According to official methods of the European Regulation/Commission Regulation EEC no. 1989/2003 (E.C. Reg. 1989/2003), several variables were measured: the free acidity, indicative of the fatty acid content, expressed as oleic acid (%); the peroxide value (PV), which is a measure of the amount of the hydroperoxides ($meqO_2/kg$) due to oxidation; and the spectrophotometric indices, i.e. the UV absorbance at 232 and 270 nm (K_{232}, K_{270} and ΔK), a measure of double bond configuration.

The carotenoid and chlorophyll determination was carried out by using a spectrophotometer (Mod. 7800 with plotter PTL 396, Jasco), using the same procedure described by Tura et al., 2007. The results have been expressed in mg of β-carotene or chlorophyll per kilogram of oil.

The fatty acid composition was determined as methyl esters following the procedures described in the enclosures of the European Commission Regulation EEC no. 2568/91 (E.C. Reg. 2568/1991). Tocopherol contents were analysed by HPLC method, using the procedure proposed by Tura et al. (2007).

2.2.2. NIR spectroscopy

NIR spectral data were collected in transmission mode using vials of 8 mm path length with an FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany). The spectral data were collected over the range from 12,500 to 4500 cm^{-1} (resolution 8 cm^{-1}, scanner velocity: 10 kHz, background: 64 scans, sample: 64 scans) at room temperature. Instrument control and initial data processing were performed using OPUS software (v. 6.5 Bruker Optics, Milan, Italy).

Table 1
Range of chemical parameters of Casaliva, Leccino, and Frantoio extra virgin olive oils.

		Monovarietal oils ($N=82$)		
		Casaliva ($n=27$)	Leccino ($n=28$)	Frantoio ($n=27$)
Acidity (%)	Range	0.14–0.82	0.11–1.23	0.17–1.46
	Mean	0.38	0.43	0.41
	S.D.	0.20	0.31	0.27
PV ($meqO_2/kg$)	Range	3.10–11.58	2.66–11.50	3.66–11.32
	Mean	7.43	5.85	6.75
	S.D.	2.42	1.80	2.25
K_{232}	Range	1.07–1.46	1.09–1.47	1.09–1.47
	Mean	1.27	1.25	1.27
	S.D.	0.11	0.10	0.11
K_{270}	Range	0.06–0.13	0.05–0.14	0.07–0.16
	Mean	0.10	0.09	0.10
	S.D.	0.02	0.02	0.02

PV, peroxide value; K_{232} and K_{270}, UV absorbance at 232 and 270 nm; S.D., standard deviation.

2.2.3. MIR spectroscopy

ATR FT-IR experiments were performed by a spectrometer (VERTEX 70, Bruker Optics, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector.

Table 2
Range of fatty acid composition of Casaliva, Leccino, and Frantoio extra virgin olive oils.

		Monovarietal oils ($N=82$)		
		Casaliva ($n=27$)	Leccino ($n=28$)	Frantoio ($n=27$)
C14:0 (%)	Range	0.01–0.05	0.01–0.024	0.01–0.40
	Mean	0.02	0.01	0.03
	S.D.	0.01	0.005	0.07
C16:0 (%)	Range	8.07–15.72	9.22–15.43	10.12–17.73
	Mean	11.72	13.28	12.54
	S.D.	2.01	1.54	1.51
C16:1is (%)	Range	0.05–0.12	0.07–0.13	0.05–0.12
	Mean	0.08	0.11	0.08
	S.D.	0.02	0.02	0.02
C16:1c (%)	Range	0.41–1.58	0.64–1.97	0.02–1.12
	Mean	0.75	1.06	0.72
	S.D.	0.32	0.41	0.25
C17:0 (%)	Range	0.02–0.11	0.02–0.05	0.02–0.08
	Mean	0.04	0.03	0.04
	S.D.	0.02	0.01	0.01
C17:1 (%)	Range	0.05–0.21	0.05–0.09	0.04–0.25
	Mean	0.08	0.07	0.08
	S.D.	0.04	0.01	0.04
C18:0 (%)	Range	1.45–2.76	1.42–2.31	1.45–2.30
	Mean	2.02	1.78	1.89
	S.D.	0.42	0.26	0.23
C18:1 (%)	Range	68.68–87.72	72.83–82.79	71.50–80.03
	Mean	76.65	77.15	76.34
	S.D.	3.60	2.32	2.35
C18:2 (%)	Range	5.25–11.54	4.08–8.43	5.07–10.27
	Mean	7.28	5.30	6.84
	S.D.	1.98	0.86	1.40
C18:3 (%)	Range	0.38–1.12	0.40–0.90	0.46–1.28
	Mean	0.67	0.69	0.71
	S.D.	0.21	0.18	0.20
C20:0 (%)	Range	0.23–0.44	0.18–0.33	0.22–0.39
	Mean	0.32	0.26	0.32
	S.D.	0.05	0.04	0.05
C20:1 (%)	Range	0.01–0.40	0.01–0.35	0.01–0.40
	Mean	0.17	0.12	0.17
	S.D.	0.14	0.12	0.17
C22:0 (%)	Range	0.06–0.16	0.04–0.13	0.05–0.14
	Mean	0.10	0.075	0.10
	S.D.	0.03	0.02	0.03
C24:0 (%)	Range	0.02–0.15	0.01–0.10	0.02–0.08
	Mean	0.05	0.036	0.05
	S.D.	0.03	0.02	0.02

S.D. = standard deviation.