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Heat-oxidation stability of palm oil blended with extra virgin olive oil

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ABSTRACT

Rancimat induction time of palm oil (PO), several extra virgin olive oils (EV) and their binary blends have been determined at three different temperatures (120, 130 and 140 °C). Analytical composition and oxidation stability of PO/EV blends were found to be a linear combination of the oil partners. Induction time of pure PO was always higher than those of EV oils and blends, in which induction time increased proportionally with the percentage of PO. However, induction time of 80% PO blend was similar to that of pure PO. Fatty acid composition appeared to be the most important factor affecting heat-oxidation stability and a saturated/unsaturated ratio near 1 was the optimally stable composition. Conversely, total phenols had a zero or negative role on the oxidative stability of the blends. Finally, in heat-oxidised oils significant losses of polyunsaturated fatty acids and formation of short-chain fatty acids were recorded.

1. Introduction

Oil obtained from the palm fruits (*Elaies guineensis*) has grown to be one of the most important vegetable oils due to its advantageous properties such as high productivity, low price, high oxidation stability, fatty acid composition and, finally, good plasticity at room temperature (Nor Aini & Miskandar, 2007). Nowadays, palm oil and palm-based fractions are widely used in various food products, such as margarines, shortenings, cooking oils, spreads, confectionery and baking fats (Laning, 1985).

The versatility of palm oil for different food applications is due to several factors. The first of which is due to its fatty acid composition, typified principally by 44% palmitic acid, 5% stearic acid, 39% oleic acid and 10% linoleic acid (Ong & Goh, 2002). The ratio between saturated and unsaturated fatty acids is about 1, so palm oil is semi-solid at normal room temperature and gives an appropriate plasticity (Borwanker, 1992; Mamat, Nor Aini, Said, & Jamaludin, 2005). For the reasons stated, palm oil has become a natural alternative to hydrogenated oils and fats that contain undesirable amounts of *trans* fatty acids and that are therefore considered unsafe for human consumption (Mensink & Katan, 1992). Palm oil, with its high smoke point and strong heat-oxidation resistance, is widely used both on its own as well as in various combinations as a frying or cooking oil (De Marco et al., 2007; Rossel, 2003). Finally, palm oil also contains about 1% of minor components, such as carotenoids, tocopherols, tocotrienols, sterols, phosphatides, triterpenic and aliphatic alcohols (Sundram, Sambanthamurthi, & Tan, 2003). Carotenoids, tocotrienols and tocopherols have nutritional importance and exert a significant influence on the oxidation stability of palm oil (Goh, Cho, & Ong, 1985; Schroeder, Becker, & Skibsted, 2006; Sundram, Thiaharajan, Gapor, & Basiron, 2002).

Commonly, food manufacturers transform original vegetable oils by a physical or chemical process with the aim being to improve their nutritional quality and technical performance. Blending of two or more oils with different characteristics is one of the simplest procedures to make new specific products (O'Brien, 2004). Recently, the use of olive oil as an ingredient in specific products has been expanding. Olive oil based products are promoted as part of the "Mediterranean Diet", which is currently viewed as making a favourable dietary contribution (Ferro-Luzzi, Cialfa, Leclercq, & Toti, 1994). Consequently, the presence of olive oil in foods, especially if it is 'extra virgin', is generally highlighted on labels since it gives a positive image in terms of consumer appeal (Bower & Saadat, 1998).

Diets with palm oil or olive oil have shown comparable health effects on the levels of cholesterol, triglycerides, HDL cholesterol, and LDL cholesterol in blood (Choudhury, Tan, & Truswell, 1995; Ng et al., 1992). Therefore, palm oil mixed with extra virgin olive oils could give new fat formulations with interesting nutritional and technological properties (Alpaslana & Karaalib, 1998; Azadmard-Damirchi & Dutta, 2008; Edem, 2002).

The oxidation stability of a blend depends strongly on those of its individual oil partners (Isbell, Abbott, & Carlson, 1999). Oxidation stability of palm oil and extra virgin olive oil is very different. The stability of extra virgin olive oil is due principally to its high

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natural antioxidant content (Del Carlo et al., 2004; Vidrih, Vidakovič, & Abramovič, 2010), while the stability of PO is due principally to its high saturation level (De Marco et al., 2007; Ong & Goh, 2002).

The main objective of this study was to evaluate the heat-oxidation stability of binary blends made with palm oil and several extra virgin olive oils. The degradation of oxidised oils and blends was also investigated.

2. Materials and methods

2.1. Oil samples and reagents

Three different extra virgin olive oils were taken directly from several local producers, while palm oil was kindly gifted by Unigra S.p.A., Conselice (RA), Italy. The palm oil was melted at 50 °C with each extra virgin olive oil in percentages ranging from 20% to 80% (w/w). The oils and blends were stored in a refrigerator at 4 °C before use.

All chemicals were of analytical grade. All standard compounds used in this study were purchased from Sigma Chemical Co. (St.Louis, Mo, USA).

2.2. Heat-oxidation by Rancimat

Oxidation induction times were measured by a Rancimat apparatus model 730 (Metrohm AG, Herison, Switzerland) on 2.5 g oil heated at three different temperatures (120, 130 and 140 °C) under a purified air flow rate of 20 L/h. At the end of the thermal treatment, some samples were set aside to cool and then stored in a freezer (−18 °C) for later analysis. With the aim being to test the antioxidant effect of pure phenols, gallic and caffeic acids and hydroxytyrosol dissolved in acetone were added to the palm oil so as to give a 100 mg/kg concentration.

2.3. Analysis of the oils

Determinations of free acidity, peroxide values and K232 and K270 spectrophotometric indices were carried out according to the European Official Methods of Analysis Regulation 2568/91 (1991). K232 (dienes conjugates) and K270 (trienes conjugates) were the extinction coefficients calculated respectively on the absorption at 232 and 270 nm wavelength by using a 1% solution of oil in isooctane and a path length of 1 cm.

Fatty acid composition was determined using a gas-chromatograph MOD-8000 (Thermoquest Instrument, Rodano, MI, Italy) equipped with a flame ionisation detector. Analysis was carried out with a Supelcowax 10 (Bellefonte, PA, USA) capillary column (30 m × 0.32 mm i.d.) under the following conditions: carrier gas He at 50 kPa; split injection system with a splitting ratio 1:40; injector and detector temperatures set at 250 and 260 °C, respectively; programmed ramp 90–240 °C at 7 °C/min; injected quantity 1 μl; cold methylation with 2 N methanolic potash; internal standard undecanoic acid methyl ester.

Short-chain fatty acids (with less than ten carbon atoms), methyl octanoate and squalene were determined simultaneously with fatty acids according to Márquez-Ruíz and Dobarganes (1996) and De Leonardis, Macciola, and De Felice (1998).

Total phenols were determined spectrophotometrically using the Folin–Ciocalteau method using gallic acid to generate a calibration line. Phenols were extracted from the oil and the blends by fourfold washing with methanol:water 80:20 (v/v). Briefly, about 6 g of oil (made liquid at 50 °C) were mixed with 4 ml of 80% methanol. After centrifugation at 4000 rpm for 10 min, supernatant was withdrawn by a Pasteur glass pipette and dried using a rotary evaporator at 40 °C, recovering separately the de-phenolised oil. Residue phenols were dissolved in 2 ml 80% methanol. Finally, the solvent was evaporated from the de-phenolised oil.

Tocopherol contents were determined by a Prostar 230 HPLC instrument (Varian, Mulgrave, AUS) on Kinetex 2.6u C18 100A reversed-phase column ((Phenomenex, Macclesfield, UK) (100 mm × 4.3 mm i.d.) with acetonitrile/ methanol (60:40, v/v) as eluting solvent at a flow rate of 1.2 ml/min. The eluent was monitored by a VIS-UV detector at 295 nm. Oil samples were dissolved in hexane (1:10, w/v) and the calibration line was prepared using α-tocopherol.

2.4. Statistical analysis

Statistical analysis was performed with 16.0 SPSS statistical software (Chicago, IL, USA). Generally, analytical determinations and Rancimat tests were carried out in three replicates, calculating the mean and standard deviation. Duncan's multiple range post hoc test was performed to analyse significant differences at the 0.01 level. The Pearson correlation test was used to determine correlations between induction time and other analytical variables of oils and blends.

3. Result and discussion

3.1. Analytical composition of oils and their binary blends

A summary of the analytical determinations carried out on palm oil (PO), extra virgin olive oil samples (EVs) and their binary mixtures (blends) are given in Table 1.

An 'extra virgin olive oil' is required in Europe to have the following regulatory limits (Union Euporea Regulation, 1996): (i) free acidity <0.8% as oleic acid, (ii) peroxide values <20 meqO_2/kg and finally, (iii) K232 e K270 spectrophotometric indexes less than 2.50 and 0.20, respectively. In this respect, all the olive oils used in this study (called EV(1), EV(2) and EV(3)) belonged to the "extra virgin" commodity class.

Free acidity was very low in all EVs, lower than 0.35%. Peroxide values showed much variability among samples and specifically they were 3.9, 7.8 and 13.1 meqO_2/kg in EV(1), EV(2) and EV(3), respectively. Finally, the data of K232 and K270 were in all cases also within the legal limits.

In PO, free acidity (0.04%) and peroxide value (0.5 meqO_2/kg) were significantly lower in comparison to those of EVs; conversely, the values of K232 (2.90) and K270 (0.84) were higher. These differences were a result of the different techniques with which EVs and PO have been produced. PO is a refined oil while the EVs are mechanically extracted oils. It is known that the refining process removes free fatty acids and peroxides from crude oils, but also causes an increase in conjugated dienes and trienes.

In the PO/EVs blends, data of free acidity, peroxide values, K232 and K270 varied proportional to the amount of PO and EVs used in the mixture.

Fatty acid compositions of PO and EVs were in agreement with their typical ranges (Ong & Goh, 2002; Sambanthamurthi, Sundram, & Tan., 2000). In PO, the saturated fatty acid (SFA) content (50.57%) was similar to that of unsaturated fatty acids (UFA) (49.43%) and the ratio SFA/UFA was calculated to be 1. Conversely, in all EVs, the SFA content was clearly lower than the UFA content and the SFA/UFA ratio was on average 0.2. The more significant differences were those observed on the palmitic and oleic acids. Palmitic acid was 44.49% in PO, while it was on average about 14% in the EVs. Oleic acid was 39.14% in PO and 69.64, 73.02 and 72.91% in EV(1), EV(2), and EV(3) samples, respectively. Conversely, the linoleic acid percentage was comparable in PO and EVs. Specifically,