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Improving olive oil shelf life with lemon essential oil

G. Arcoleo*, M.C. Indovina*, G. Varvaro* C. M. Lanza**A. Mazzaglia**
* Department ITAF (Engineer and Agro-Forestry Technologies), University of Palermo
** Department DOFATA – Food Technology section, University of Catania

The aim of this research was to study the effects of the cold pressed essential oil of lemon (*Citrus Limon* L.Burm.f.) on the shelf life and sensory profile of virgin olive oil. Essential oil at 0.4 and 0.8 percentage were mixed in VOO and the evolution of flavoured oils was monitored during storage (ten months) and compared with control sample. The flavoured oils showed a greater oxidative stability that the control sample and a pleasant flavour for all considered period. The flavoured oil with essential oil of lemon could be to put on the market as alternative oil for no cooking use in order to preserve its sensorial characteristic

1. Introduction

Virgin olive oil (VOO) is one of the pillars of the Mediterranean diet and of the most modern dietary guideline for its high nutritional value. It is a functional food for its favourable fatty acid composition and for the presence of minor component with asserted antioxidant power. Oleic acid is about 70% of the total fatty acids, there are essential fatty acids and minor components such as α-tocopherol, phenolic compounds and carotenoids that prevent the formation of free radicals. During storage its nutritional and health properties may be spoiled by oxidative phenomena that can make oil unsuitable for consuming. The degrading reactions rate depends on the unsaturation grade of the fatty acids, on the presence of antioxidant and pro-oxidant compounds and on the storage conditions (Servili M. *et al.* 2004). Following the actual trend in using natural antioxidant products from vegetables, we have tested the possible use of essential lemon oil as antioxidant in order to improve food shelf-life as well as flavouring of VOO. Small amounts of cold pressed lemon essential oil were added to VOO and the chemical parameters and sensory characteristics features were periodically determined for both flavoured and not-flavoured olive oils in order to follow their evolution during the course of time. Italy is the first European producer of lemon derivate, about 60% of the lemon production is addressed to the processing industry (FAO database) and the cold pressed essential oil is regarded as the best one in the world for the peculiar smell characteristics. It is widely used as fragrance in perfumery and as flavouring in food and drinks. Several researches have shown that lemon essential oil has antioxidant properties, essentially due to monoterpenes, and antimicrobial activity thanks to their hydrophobic nature (Conte A. *et al.* 2006). This

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research has been carried out to contribute to improve the shelf life of VOO and to wide the uses of essential lemon oil producing flavoured olive oils. The flavoured vegetable oils currently on the market are obtained with the maceration of citrus peel and flavedo and albedo components could be found in the oils. The production of flavoured oils using essential oils is also interesting because the flavouring process can be adjusted according to vegetable oils features.

2. Materials and methods

Essential oil**.** The used cold-pressed essential oil was obtained from fruits of *Citrus Limon* L. Burm. f. processed by an FMC In-Line system at "Agrumaria Corleone srl" factory (Palermo, Italy). It was a winter sample and was taken out from a stainless steel tank containing essential oil that was obtained between December 2007 and January 2008.

Virgin olive oil. It was obtained from Nocellara del Belice cultivar during the 2007/2008 olive-oil year. The olives were processed by traditional three-phases decanter at "Goccia D'Oro" mill in Menfi (Agrigento, Italy). Oil sample collected at the end of the production cycle was poured into a stainless steel tank.

Lemon flavoured oil. After conditioning VVO sample was divided into three parts and two of them were flavoured with lemon essential oil at 0.4 and 0.8 percentage.

Experimental design. The VOO sample (control) and the flavoured oils were poured into amber bottles and stored in a dark cellar at temperatures ranging from 10°C (in winter) to 22°C (in summer), simulating the homely oil preservation. Periodically the flavoured samples and the VOO sample were analyzed in order to determine their chemical and sensory parameters. Each chemical test was repeated three times. The statistical package STATGRAPHICS Plus version 4.0 was used in order to generate mean, standard deviation, and one way Analysis of Variance (ANOVA). Sensory data were analyzed for each attribute and the significance was tested with F test. The mean values were submitted to the multiple comparison test using the procedure LSD (Least Significant Difference) that allows to determine what attributes differentiate the samples.

The first samples (I)were tested on 18th February (t=0), the other five samples were tested on 27th March (II), 19th May (III), 23rd July (IV), 24th October (V) and 18th December (VI).

2.1 Lemon essential oil analyses:

Residue. The residue, expressed in percentage, was determined after evaporation of essential oil at 100°C.

Residue composition. Non-volatile fraction analysis was carried out with an HPLC Perkin-Elmer series 200 equipped with a Chrompspher 5 Si (250 x 4,6 mm) according to Dugo G. *et al.* (1999).

Volatile fraction**.** Gas chromatographic analysis was carried out with GC/MS Agilent 6898 series equipped with a DB5 column (length 30 m and internal diameter 0.25 mm) according to Dugo G. *et al.* (1999). Component identification was carried out using MS information, linear retention indices (LRI) and co-injection with commercial standards

Radical Scavenging Activity**.** The free stable radical DPPH° (2.2'-Diphenyl-1-picrylhazyl) was used to measure radical scavenging activity of essential oil samples.

W. Brand-Williams *et al.* (1995) method was used. After 30 minutes of incubation at 25°C with continuous shaking in dark, the absorbance was measured at 515nm using a Beckman DU-640 spectrophotometer. Radical scavenging activity (RSA) was measured as free radical DPPH inhibition percentage. RSA% = $(A_{blank} - A_{sample})/A_{blank} * 100$, where A_{blank} was the absorbance of the control reaction.

Superoxide anion Scavenging Activity. The Superoxide anion Scavenging Activity of essential oil was measured using xanthine-xantine oxidase method (Halliwell B. *et al.*1992) with NBT as indicator. After 90 min of incubation at 25°C with continuous shaking in dark, the absorbance of formazan chromofore at 560nm was measured against a control solution. In order to rectify the base line, solution in which hypoxantina was replaced by buffer solution was also prepared. The Superoxide anion Scavenging Activity was measured as the decrease of absorbance at 560nm. This was possible because it was verified that the essential oil does not inhibit the xantina oxidase. SSA (%) = $(A_0 - A_1)/ A_0 * 100$, where A_0 and A_1 where the absorbance of the control and sample.

2.2 Olive oils analyses:

Free fatty acid (FFA), Peroxides index (PI), UV parameters (K232, K270), and the methylic esters were obtained according to the official method set out by Reg. EEC. n. 2568/91 del 1991. The fatty acid composition was carried out using Arcoleo et al (2006) method. Total phenol (TP) content was determined following the procedure indicated by G. Montedoro *et al.* (1992). The α-tocopherol was determined according to method P. Rovellini *et al.* (1997). Carotenoids and chlorophylls contents were determined in solution oil at 20% in hexane. The absorbencies at 435 nm and 670 nm for carotenoids and chlorophylls respectively were measured and the coefficients of extinction in hexane reported in literature (G. Modi *et al.*, 1992) were used for quantitative analysis.
The induction time (oxidative stability) was measured by Rancimat test. The air flow was 20L/h and temperature 120°C.

2.3 Sensory analysis:

In order to define the attributes characterizing the products and to investigate the sensory changes of samples during the storage period (ten month), the sensory profile method (ISO 13299, 2003) was applied. Some preliminary sessions have been necessary to set, with a panel of trained judges (10), a common vocabulary. In the first executive phase, in plenary session, the judges identified the sensory attributes (olfactive, taste, mouth feel) more meaningful for the product to evaluate. On the basis of the frequency of elicitation (>50%), 18 sensory attributes were considered as reported in the spider plot. Judges were requested to evaluate, in the sensory laboratory (UNI ISO 8589, 1990) of Food Technology Section of DOFATA) equipped with a specific software (FIZZ Biosystèmes), the intensity of the sensory attributes by assigning a score between 1 (absence of the sensation) and 9 (extremely intense). The samples have been evaluated by judges in blue glasses, according to COI (International Council of Olives) for the sensory evaluation of olive oil. The results reported in this work are referred to t=0 (I) and to 10th month (VI) of storage.

3. Results and discussion

The values of initial parameters of virgin olive oil (Tab.1, Fig. 2) are about the average value for oils obtained with three-phases decanter. Chemical and sensory indexes show a good quality VOO. However the linolenic acid content is on the verge of law: this can be found frequently in olive oils from Nocellara del Belice cv. In the volatile fraction of lemon essential oil 64 components were identified and a summary is reported. Citral content of lemon essential oil was 2.29% of volatile fraction. Limonene (67.29%), β-pinene (10,98%), γ-terpinene (9,24%), α-pinene (1,89%), myrcene (1,60%) were the major monoterpenes. These are unsaturated compounds that can easily be oxidized to peroxides. Other antioxidant compounds are in the residue as flavonoid, phenols, cumarins, carotenoids. For this reason the use of small account of lemon essential oil can protect VOO from oxidative processes. The addition of cold pressed essential oil caused significative changes in the storage evolution between the flavoured oils and the control. Initially at t=0, significative differences were observed only for sensory parameters. In particular, at t=0, for four sensory attributes: Olive odour ($p \leq 0.05$), Lemon Odour, Lemon juice odour, Lemon peel odour ($p \leq 0.001$). Chemical and physical indexes evolution during storage is showed in fig.1. The degree of oxidation of the control sample was more advanced than flavoured oils. In the flavoured sample PI is always less than 20 $mEqO_2/kg$ (limit by law) because the presence of essential oil in VOO lengthened the induction period. In the control the trends of K_{232} and PI were similar. The initial phase of oxidation was observed and these parameters increased because the formation of peroxides predominated to their destruction. They reached the maximum values after the summer and then a decrement was observed. Significative differences from flavoured samples and control were found ($p<0.05$) from third sampling (III). No significative differences were observed from the flavoured sample at 0.4% and at 0.8%. In the control, K_{270} value increased at the end of storage because the aldehydes, ketones and other carbonyl compounds were produced by degradation of the hydroperoxides. This oxidative evolution was little observed by sensory analysis: during the storage period the three trials of oil samples (control, 0.4 and 0.8 % of lemon oil) showed a similar behaviour with regard the sensory attributes that appeared very stable with few significant differences. Significant differences for the attributes Lemon Odour, Lemon juice odour, Lemon peel odour for $p \leq 0.001$ were observed even at the end of storage, while no significative difference of Olive odour attribute was observed. Probably this was correlated to final ossidative state of control sample. Fig.1 shows that essential oil protected the α-tocopherol, first line of defence against photo-oxidation. Significative difference for $p< 0.05$ were showed between the control and flavoured oils since the third sampling. The total phenol content decreased for all samples with more accentuate trend for the control one, significative differences were found at V and VI sampling. FFA, fatty acid composition and pigments showed no significative differences.

4. Conclusions

The use of small amounts of lemon cold pressed essential oil improves the shelf life of VOO because the oxidative stability of flavoured virgin olive oil increases. Regarding

the flavouring, the judges valuated good acceptability for both essential oil percentages (0.4 and 0.8). It is therefore possible to put on market this alternative product that can be used like condiment of meat, fish, vegetables and other food; however, in order to preserve its sensory characteristics, it will be not suitable for cooking.

Table 1 – Olive oil initial parameters

	mean		st.dev.	**Fatty acid composition (%)**	mean		st.dev.
FFA (% oleic acid)	0.22	±	0.020	**C 16:0**	9.88	±	0.40
PI (meq O_2/kg)	7.7	±	0.525	**C 16:1**	0.46	±	0.02
K_{232}	1.93	±	0.007	**C 17:0**	0.05	±	0.00
K_{270}	0.11	±	0.010	**C 17:1**	0.08	±	0.00
ΔK	-0.002	±	0.001	**C 18:0**	2.63	±	0.11
Chlorophylls (ppm)	10.6	±	0.248	**C 18:1**	75.27	±	0.24
Carotenoids (ppm)	4.5	±	0.046	**C 18:2**	9.78	±	0.40
Total PolyPhenols (ppm GAE)	291	±	12	**C 20:0**	0.29	±	0.15
α-tocopherol (ppm)	186	±	2	**C 20:1**	0.48	±	0.23
Induction Time (h)	7.32	±	0.140	**C 18:3**	0.98	±	0.21
C18:1/C18:2	7.55	±	0.330	**C 22:0**	0.1	±	0.01
				C 22:1	0	±	0.00
				C 24:0	0.01	±	0.01

Table 2 – Lemon essential oil parameters

Volatile fraction	(% area)	**Non-volatile fraction**	(% area)
Monoterpenes	94.29	bergamottin	26.05
Alcohols	0.48	5geranioxi7metoxicumarin	18.38
Aldheids	2.54	5isopentoxi7metoxicumarin	0.78
Citral	2.29	8geranioxipsoralene	4.07
Aldheids exept Citral	0.25	citroptene	18.85
Total Esters	0.83	ernarin	0.18
Total Sesquiterpenes	1.35	imperatorin	1.81
		fellopterin	1.72
Residue (%)	2.31	oxipeucedanin	16.56
RSA (%)	19.85	1,4-biancangelicol	0.52
SSA (%)	24.82	1,5-oxipeucedanin hydrate	8.19

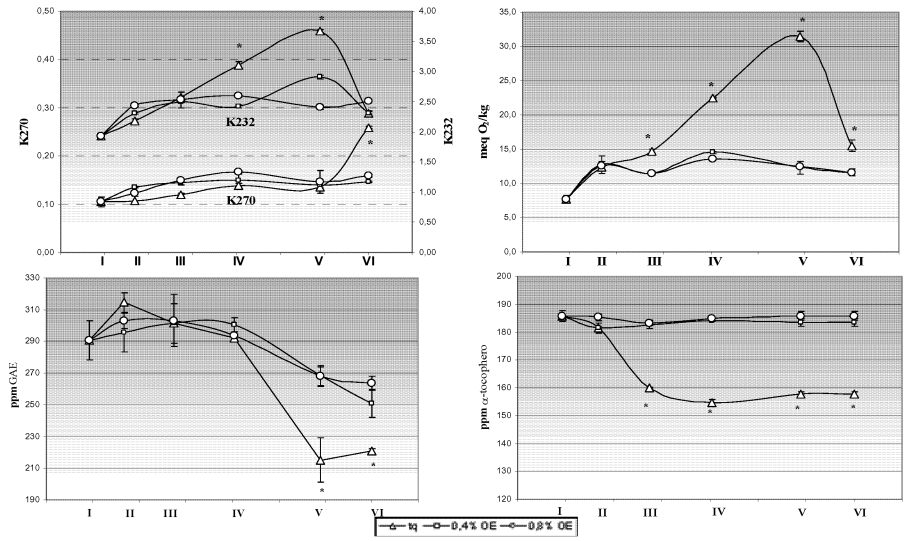

Figure 1 – K232, K270, PI, TP and α-tocopherol evolution during storage

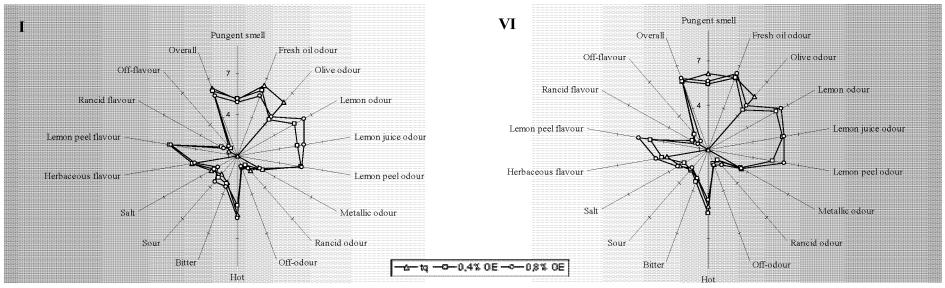

Figure 2 - Sensory analysis of samples at beginning (I) and end (VI) of storage

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