

INVESTIGACIÓN

Hydrolysis and oxidation of covering oil in canned dried tomatoes as affected by pasteurization

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RESUMEN

Hidrolisis y oxidación del aceite de cobertura en tomate desecado enlatado durante la pasteurización.

Los efectos de la pasterización sobre la calidad química del aceite de oliva virgen extra de cobertura en tomates desecados enlatados han sido estudiados durante su almacenamiento a través de determinaciones analíticas convencionales (acidez, índice peróxidos, índice de p-anisidina, índices espectrofotométricos) y no convencionales (compuestos polares). Todos los análisis realizados muestran que el aceite de oliva virgen extra de las muestras pasterizadas sufre una degradación hidrolítica ligeramente mayor que el de las no tratadas pero resulta menos oxidado que el aceite de las muestras no tratadas.

PALABRAS-CLAVE: *Aceite de oliva virgen extra - Compuestos de la reacción de Maillard - HPSEC - Oxidación - Vegetales enlatados.*

SUMMARY

Hydrolysis and oxidation of covering oil in canned dried tomatoes as affected by pasteurization.

The effects of pasteurization on the chemical quality of the extra-virgin olive oil used as a covering for canned dried tomatoes were studied during storage through conventional (acidity, peroxide value, p-anisidine value, spectrophotometric indexes) and non conventional (polar compounds) analytical determinations. All the performed analyses show that extra-virgin olive oil from pasteurized samples underwent hydrolytic degradation slightly more than unheated ones but resulted slightly less oxidized than oil from untreated vessels.

KEY-WORDS: *Canned vegetables - Extra-virgin olive oil - HPSEC - Maillard reaction compounds - Oxidation.*

1. INTRODUCTION

Oxidative and hydrolytic reactions taking place in the covering oil of preserved foods have been poorly studied (Cucurachi, 1966; Paganuzzi et al., 1995; Bizzozero and Carnelli, 1996; Cavallaro et al., 1996; Mucciarella and Marsilio, 1997; Gomes et al., 1998).

In particular, the effects of process and storage on oil chemical parameters were considered. Paganuzzi et al. (1995) reported the results of the analytical determinations performed on the covering oil of preserved foods packaged in glass vessels. In some of the analyzed samples, chemical parameters such as percentage of free fatty acids, peroxide value and spectrophotometric indexes were higher than the European legal limits (2568/91 EEC Regulation) already after a few months of storage.

Caponio et al. (2003a) investigated the oxidative and hydrolytic degradation of the covering oil of preserved mushrooms. They found that the HPSEC analysis of polar compounds and the analysis of trans-isomers could be suitable for ascertaining the oil quality. A similar study was performed on the covering oil of preserved artichokes (Caponio et al., 2003b). The routine analyses (free fatty acids, peroxide value, etc.) did not allow investigators to express a judgement about the quality and the genuineness of the different oils used (extra-virgin olive oil, olive oil, sunflower oil). On the other hand, the determination of the polar compounds (triglyceride oligopolymers, oxidized triglycerides, diglycerides) and trans-isomers allowed distinguishing among the different oils.

Analogous results were obtained by extending these studies to other in-oil preserved vegetables (Caponio et al., 2003c) and fish (Caponio et al., 2002; 2003d). In the case of the covering oil of preserved tuna, the acidic composition showed the presence of highly unsaturated fatty acids, typical of fish lipids. Trans-isomers were always absent from extra-virgin oils and always present in olive oils and refined seed oils. Polar compounds were present in an increasing order in extra-virgin olive oils, olive oils and refined seed oils.

The aim of this work was to evaluate the effects of pasteurization on the oxidative and hydrolytic degradation of covering olive oil in preserved dried tomatoes.

2. EXPERIMENTAL

2.1. Preparation of in-oil canned tomatoes

The sample preparation was carried out according to traditional recipes. Dried salted tomatoes were previously blanched in boiling white vinegar for 30 seconds, then drained, dried and put in transparent glass vessels, supplied with metal caps, of 280g capacity. Vessels were filled in with extra-virgin olive oil obtained by cv. «Coratina» olives and hermetically sealed (tomatoes:oil, 60:40 w/w). Half of the samples were submitted to pasteurization (74°C, 15 minutes in the core), which is the heat treatment recommended by the Food and Drug Administration (2002) for canned foods having pH lower than 4.6, and then quickly cooled to room temperature. The remaining samples were not heated as usually occurs in domestic preparation. Twenty-four vessels were prepared.

Storage was carried out for 12 months at room temperature (about 20-25°C), in order to simulate retail (dark/light) conditions.

2.2. Analyses

The covering oils were separated from the vegetable matrix at different storage times, filtered on anhydrous sodium sulphate and stored in glass tubes with screw caps at -20°C up to the analysis. The original extra-virgin olive oil was also analyzed.

The following analyses were carried out:

Acidic Composition, $C_{18:1}$ and $C_{18:2}+C_{18:3}$ trans-isomer contents. The methyl-esters of fatty acids were prepared according to the 2568/91 EEC Regulation and submitted to gas-chromatography analysis. The gas-chromatographic system consisted of a GC 8560 Mega 2 (Fisons Instruments, Milan, Italy) equipped with a WCOT fused silica capillary column (Chrompack, Middelburg, Holland), 25m, 0.32mm i.d., 0.5µm film thickness. Oven temperature was kept at 200°C. An FID detector, connected to an integrator, was used ($T = 300^\circ\text{C}$). The carrier was helium at a flow rate of 2ml/min. The peaks on the chromatograms were identified by methyl-ester standards (Sigma Chemical, St. Louis, MO). The trans-isomer analyses were carried out using a Silar 10 capillary column (Chrompack, Middelburg, Holland), 50m, 0.32mm i.d., 0.20m film thickness, at the gas-chromatographic conditions reported in the 1429/92 EEC Regulation.

Acidity, expressed as g of oleic acid per 100g of oil, according to the Cd 3d-63 Official Method of the AOCS (1993);

Peroxide Values (P.V.), expressed as milliEquivalents (mEq) of active oxygen per kg of oil, according to the Cd 8-53 Official Method of the AOCS (1993);

Spectrophotometric Indexes (K_{232} , K_{270} and ΔK), according to the Ch 5-91 Official Method of the AOCS (1993);

p-Anisidine Values (p-A.V.), according to the 2504 IUPAC method (1987);

Polar Compounds (PC), according to the 2507 IUPAC method (1987). PC were submitted to high-performance size-exclusion chromatography (HPSEC) to determine oligopolymers, oxidized triglycerides and diglycerides. The chromatographic system consisted of a Perkin-Elmer pump, series 10, a 7125 S sample injector (Rheodyne), a 50µl injector loop and a series of three PL-gel columns (Perkin-Elmer Ltd., Beaconsfield, U.K.) of 0.75mm i.d. x 30cm length. The columns were packed with highly cross-linked styrene divinylbenzene copolymers with a particle diameter of 5m and pore diameters of 500, 500 and 100Å, respectively. A PL-gel guard column (Perkin-Elmer Ltd.) of 7.5mm i.d. x 5cm length was used. The detector was a differential refractometer (refractive index detector, RID-6A, Shimadzu Corp., Osaka, Japan) connected to an integrator. The elution solvent was CH_2Cl_2 for HPLC (purity = 99.9%, supplied by Baker, Deventer, Holland) at a flow rate of 1.0ml/min. Peaks on the chromatograms were identified and quantified according to Gomes (1992) and Gomes and Caponio (1999).

Analyses were carried out at least in duplicate and the difference between the two performed on the same sample did not exceed 6%.

3. RESULTS AND DISCUSSION

Table I shows the acidic composition of the original extra-virgin olive oil. The fatty acid composition was in accordance with the «Fat and Derivative Rules» fixed by the «Stazione Sperimentale per le Industrie degli Oli e dei Grassi» in Milan (Italy) (1994). Furthermore, miristic, linolenic, arachic, eicosenoic, beenic and lignoceric acid contents were below the European upper legal limits (EEC Reg. 2568/91). Trans oleic isomer were present at trace levels in extra virgin olive oil used as covering medium after 12 months of storage and did not change after heat treatment or during the storage period and may thus be used to ascertain the genuineness of the oil. Trans linoleic and trans linolenic isomers were not detected neither in the original extra-virgin olive oil nor after one year of storage.

Acidity increased without great differences among oils from pasteurized samples and oils from the untreated ones, ranging from 0.27 to 0.51g/100g for pasteurized oils and 0.54 g/100g for the untreated ones after 12 month-storage (Fig. 1). Acidity values can also be considered satisfactory after 12 months of storage, because their results were lower than both the upper European legal limit for the

Table I
Acidic composition of the original extra-virgin oli-

Fatty Acids	Original extra-virgin olive oil
C _{14:0}	traces
C _{16:0}	13.23
C _{16:1}	1.05
C _{18:0}	1.90
C _{18:1}	75.96
C _{18:2}	6.62
C _{18:3}	0.68
C _{20:0}	0.40
C _{20:1}	0.10
C _{22:0}	0.02
C _{24:0}	0.04

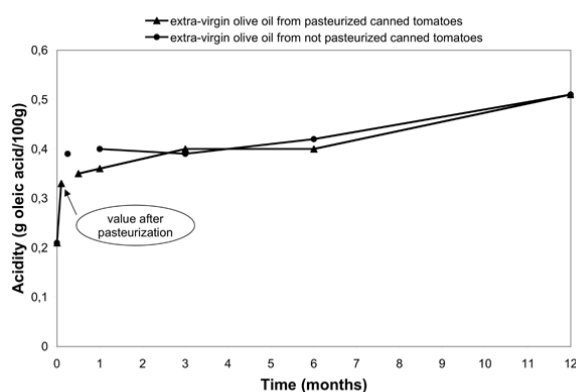


Figure 1
Acidity, expressed as g of oleic acid/100g of fat, of extra-virgin covering oils from pasteurized and not pasteurized samples.

extra-virgin olive oil (1.0g/100g) currently in force (2568/91 EEC Regulation) and the limit of 0.8 /100g fixed by the 1513/2001 EC Regulation in force from November 1st, 2003. These results depend on both the good quality of the oil used and the application of a suitable pasteurization thanks to which over-heating was avoided.

Fig. 2 shows the trends in peroxide value of oils from both pasteurized and unheated samples. For samples which did not receive the heat treatment, peroxide value increased up to a maximum (reached at 3 months of storage) and, then, decreased. This behavior can be explained by the initial increase in hydroperoxides (odorless, flavorless compounds, produced during the primary step of oxidation) and their successive breaking down to give aldehydes and ketones responsible for off-flavors (secondary oxidation) and non volatile compounds such as oligopolymers, cyclic compounds. For oils deriving

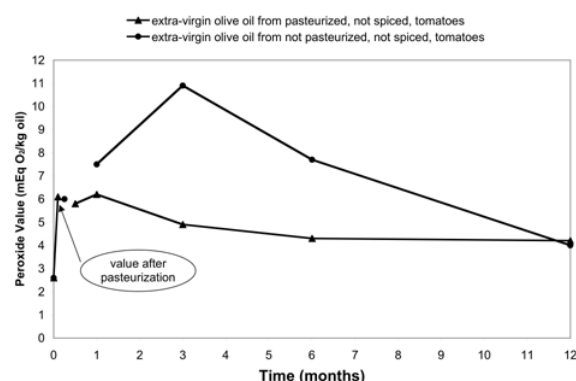


Figure 2
Peroxide value, expressed as mEqO₂/Kg of fat, of extra-virgin covering oils from pasteurized and not pasteurized samples.

from pasteurized samples, the initial increase in peroxide value was moderate and thus the successive decrease. Peroxide values of all samples were always lower than the European legal limits (2568/91 EEC Regulation) fixed for the extra-virgin olive oil (20mEqO₂/Kg) probably thanks to the high content in polyphenols (natural antioxidants) of the extra-virgin olive oil of cv. «Coratina».

Trends in secondary oxidation were measured through the evaluation of aldehyde and ketone formation (p-A.V.). Fig. 3 shows higher p-Anisidine Values for oils from heated samples up to 6 months of storage; then the trends resulted inverted.

Fig. 4 reports the spectrophotometric indexes calculated at 232 (absorbance peak of double conjugated bonds) and 270nm (absorbance peak of triple conjugated bonds), that represent further indicators of primary and secondary oxidation, respectively. During storage, the increase in the spectrophotometric indexes was very low for both the oils.

The percentages of total polar compounds and their different classes are reported in Table II. Triglyceride oligopolymers, absent from the extra-virgin olive oil used to fill in the vessels compared in traces at 3 months of storage with negligible differences between pasteurized and unheated samples. A slightly higher tendency to oxidation of oils from unheated samples seemed to be observed in Fig. 5 which shows the trend of the sum oligopolymers-oxidized triglycerides.

However, in all the samples, the percentages of oxidation and hydrolytic compounds are too low to prove a restrained degradation progression. In particular, it is quite evident that most parameters increased faster during the first months of storage, and then hydrolytic degradation and oxidation slowed down. These results explain the long shelf life of in-oil canned vegetables.

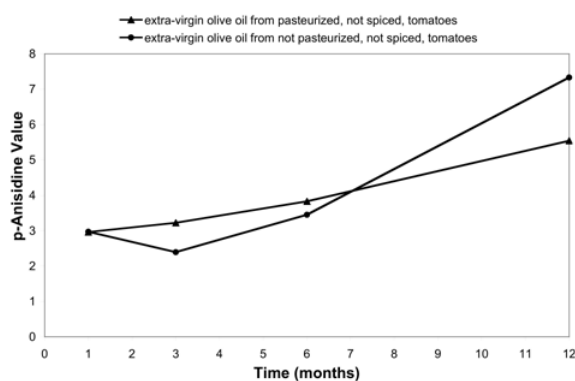


Figure 3
p-Anisidine value of extra-virgin covering oils from pasteurized and not pasteurized samples.

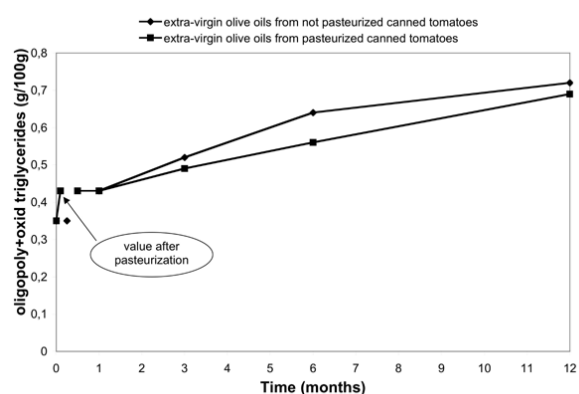


Figure 5
Oligopolymers+oxidized triglycerides in the extra-virgin covering oil

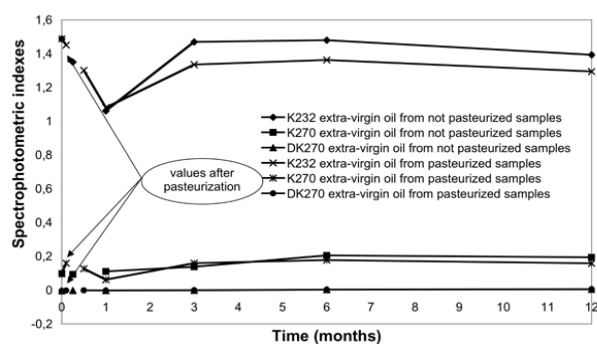


Figure 4
Spectrophotometric indexes of the extra-virgin covering oils.

to investigate the effect of pasteurization on the hydrolytic and oxidative state of oils. Under the applied experimental conditions, pasteurization induced only a small increase in hydrolytic degradation. In general, low oxidation and hydrolytic levels were observed. This could be due to the mild heat treatment applied and to the packaging and storage conditions (room temperature, containers showing a total barrier against oxygen, scarce oxygen available for degradation reactions since vessels were completely filled with oil). Furthermore, the choice of a good quality oil and the employment of small-sized vessels (to avoid a prolonged heat treatment which could have a pro-oxidant effect instead of an antioxidant effect) allowed the final product to have a real and not only nominal shelf-life.

4. CONCLUSIONS

High-performance size-exclusion chromatography together with conventional analytical determinations can be considered a suitable and reliable technique

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Table II
Total polar compounds and their different classes expressed as g/100g

Total Polar Compounds	Oligo-polymers	Oxidized Triglycerides	Diglycerides	Free Fatty Acids	Others		Total Polar Compounds	Oligo-polymers	Oxidized Triglycerides	Diglycerides	Free Fatty Acids	Others
Extra-virgin olive oils from pasteurized canned tomatoes							Extra-virgin olive oils from not pasteurized canned tomatoes					
2.43	0.00	0.35	1.59	0.21	0.28	0	2.43	0.00	0.35	1.59	0.21	0.28
2.69	0.00	0.43	1.60	0.33	0.33	After pasteuriz.						
						After a week	2.49	0.00	0.35	1.48	0.39	0.27
2.73	0.00	0.43	1.65	0.35	0.30	After 2 weeks						
2.74	0.00	0.43	1.65	0.36	0.30	After a month	2.72	0.00	0.43	1.60	0.40	0.29
2.86	0.02	0.47	1.69	0.40	0.28	After 3 months	2.92	0.01	0.51	1.65	0.39	0.26
2.90	0.05	0.51	1.73	0.40	0.21	After 6 months	2.99	0.05	0.59	1.67	0.42	0.26
3.31	0.08	0.61	1.85	0.51	0.26	After 12 months	3.18	0.09	0.63	1.72	0.51	0.23

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