High Pressure Effects on Lipid Oxidation of Extra Virgin Olive Oils and Seed Oils

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Abstract

High pressure treatment was applied to extra virgin olive oils and to seed oils in order to verify if and to what extent modifications in the lipidic fraction can occur. Six different extra virgin olive oils and five different seed oils(grape-stone, sunflower, soybean, peanut, maize) were treated at 700 Mpa for 10 minutes at room temperature. Different analytical parameters (peroxide value, para-anisidine value, rancimat test, volatile hydrocarbons) were measured to study the oxidative stability of the treated oils. The application of high pressure at these operating conditions produced changes in the p-anisidine values, but not in the peroxide values and volatile hydrocarbons of the oil samples. As expected, in all cases, the olive oils were more resistant to oxidation than the seed oil samples. It is necessary to point out that the effects of high pressure treatment on oils depend on their origin, composition, initial quality and age.

Introduction

Studies on the applications of high pressure technology in food processing have been carried out recently, not only to sterilize, but also to inactivate enzymes and to modify some functional characteristics of foods (fish, meat, cereals, milk, fruit, beverages) (TAUSCHER, 1995; CHEFTEL, 1991). Several pressurized fruit-based products (jams, yorgurts, juices) have appeared on the market in Japan over the last few years (PALMIERI et al., 1992).

A number of studies have been carried out on the effects of high pressure on micro-organisms (BUTZ and LUDWIG. 1986; KNORR et al., 1992; OGAWA et al., 1990; GOLA et al., 1992), enzymes (NICOLI et al., 1994; ASAKA and HAYASHI, 1991; ANESE et al., 1995) and food components such as proteins (HEREMANS, 1982; MASSON, 1992; PITTIA et al., 1995) and starch (HAYASHI and HAYASHIDA, 1989), but there are few papers concerning the modification of the lipidic fraction of pressurized foods.

TANAKA et al. (1990) studied freeze-dried sardines and sardine oils treated at 180 Mpa for 60 minutes. In this case, the medium pressure treatment produced the formation and an increase in oxidation products in the oil of the freeze-dried sardines compared to the oil only. Nevertheless lipid oxidation occurred only during the subsequent storage time at 5° C in the dark, probably due to the iron present in the non-oil fraction, which acts as a catalyst.

OSHIMA et al. (1993) reviewed recent studies on the effect of high pressure processing in properties of foods, in particular of fish and fish products. They considered the effects of the high pressure treatment on the appearance, proteins, enzyme activities, bacteria and fat oxidation. One of the disadvantages of this process carried out on fish products is the accelerated lipid oxidation.

KOWALSKY et al. (1994) studied the high pressure effects on lipid oxidation of linolenic acid. Samples treated for the same time and temperature at atmospheric pressure. During the first step of the reaction there was an increase in the oxidation products (hydroperoxides with an adsorbance maximum at 234 nm); on the other hand, the subsequent lipid oxidation steps were inhibited by the treatment.

CHEA and LEWARD (1995) carried out a study in rendered pork fat under different processing conditions (pressure intensity, Aw and treatment temperature, Aw and storage temperature). According to their results, it appears that the application of pressure to pork lipids leads to a partial destruction of the peroxides in the fat with inhibitory effects at Aw above 0.55. On the other hand, the range of water activity between 0.4 and 0.55 and the presence of free iron and copper in the samples could lead to perooxidant effects.

The aim of this study was to investigate the oxidative stability of the lipid fraction present as a component of or as an ingredient in pressurized foods. A preliminary study of several olive oil and seed oil samples with different chemical characteristics was carried out.

Materials and Methods

Six different extra virgin olive oil and 5 seed oil samples were chosen. The olive oil samples (A,B,C,D,E) having different ages and storage histories (about 1 year from production occasional contact with air, storage at low temperature and in the dark) were supplied by the "*Consorzio Productorri Olive del Triveneto*", While olive oil sample F and the seed oils (grape-stone, sunflower, soybean, peanut, maize) were bought on the market. The five non fresh extra virgin olive oil samples were purposely chosen to simulate the usual processing conditions that could be presumably adopted by a food industry.

Aliquots of 50 g of the oil samples were placed in thermos-sealed flexible plastic containers (nylon/PE films -100 mL) and treated at 700 Mpa for 10 minutes at room temperature. The high pressure treatment was done at the SSICA (Stazione Sperimentale Industria Conserve Alimentari, Parma, Italy) using a pilot plant Asea Brown Boveri Hydrostatic pressure QFP-6 (ABB Industria, Milano, Italy).

An aliquot of soybean oil was placed in vials (25 mL) which were then hermetically closed with butyl septa and metal caps and heat treated at 120° C in an air circulating oven.

Immediately after the treatment, the following analytical parameters were measured:

Peroxide value (POV): expressed as mEq of active oxygen per kg of oil, according to the AOAC method (1984).

Para-anisidine value (AV): using the NGD methods (1980).

Rancimat test as a storage test: a mod. 679 Metrohom Rancimat (Metrohom, Herisau, Switzerland) was used. Aliquots of 5 g of sample were placed in the reaction tubes and the test was carried out at 110° C with an air flow of 20 L/h. For each position of the wet section, the temperature of the sample was measured with a thermometer to correct the heating system (temperature fluctuation < 0.2° C); the chart speed was 1cm/h. The oxidation curves obtained from the Rancimat test describe the resistance of the oil to oxidation (SEVERINI and LERICI), 1985). The oil stability is expressed as "induction time" (hours) as suggested by LAUBLI and BRUTEL (1986).

Volatile hydrocarbons were determined by headspace gas-chromotographic analysis (HS-GC) (LOLIGER, 1990). Two gram samples were placed in vials (10mL) which were then hermetically closed with butyl septa and metal caps. A 2-m glass packed column (4 mm ID) filled with F-1 180-250 mm alumina on a Carlo Erba GC 6000 Vega Series (Carlo Erba Instruments, Milano, Italy) gas chromatograph, equipped with a flame ionisation detector (FID) was used. The operating conditions were as follows: Column temperature programmed from 80° to 250° C with an increasing rate of 12° C / min and then held isothermally at 250° C for 15 min; detector oven temperature, 250° C; injector temperature, 200° C; carrier gas (N2) flow rate, 30 mL/min. The gas chromatograph was connected to a Head Space Autosampler mod. 250 (Carlo Erba Instruments, Milano, Italy) equipped with a Gastight 1750 syringe (Hamilton, Bonaduz AG, Bonaduz, Switzerland). The vials were heated at 40° C before withdrawing the headspace gas. The volume injected was 0.2 mL. A Shimadzu Mod. CR 1B (Tokyo, Japan) integrator was used to record the chromatograms.

All the samples were stored at -18° C and analysed again after 1 year. For these sample only peroxide and P-anisidine values were determined.

Preliminary analyses (in duplicate) of the olive samples were carried out in order to obtain a profile of their chemical characteristics:

- Total phenolics (Folin Ciocalteau), following the method of MONTEDORO and

Table 1. Some chemical characteristics of the seed oil samples reported on the packaging information.

Seed oils	Saturated/ unsaturated fatty	Added Tocopherols (ppm)
grape-stone	0.11	/
Sunflower	0.08	/
Soybean	0.17	640
Peanut	0.24	/
Maize	0.20	600

Table 2. Some chemical characteristics of extra virgin olive oil samples

Olive oils	Saturated/Unsaturated fatty acids	Phenolics (ppm)	Tocopherols (ppm)
A	0.16	286.3	131.6
B	0.16	266.4	190.4
C	0.14	62.2	154.6
D	0.15	172.2	197.8
E	0.12	142.5	157.4

Table 3. Peroxide values (POV) (±standard deviations), expressed as mEq of O_2 /kg of oil, of the olive oil and seed oil samples before and after high pressure traetment at 700 Mpa for 10 minutes at room temperature. The values were determined immediately after treatment (T=0) and after 1 year of storage at -18° C (T=1).

Sample	Peroxide Value			
	Raw T=0	Raw T=1 year	HP T=0	HP T=1 year
Olive oils				
A	6.08± 0.02	6.02± 0.18	5.97± 0.04	5.49± 0.15
B	14.68± 0.41	14.14± 0.02	13.57± 0.25	15.58± 0.79
C	6.96± 0.2	6.86± 0.14	7.49± 0.01	6.95± 0.05
D	14.17±0.15	13.67± 0.25	13.95 ±0.07	14.20± 0.03
E	15.6 ± 0.54	14.62± 0.42	16.83± 0.47	14.11± 0.85
F	5.00± 0.42	5.36± 0.1	5.79± 0.04	5.69± 0.4
Seed Oils				
grape-stone	1.04± 0.1	2.11± 0.02	1.38± 0.25	2.42± 0.01
sunflower	0.88± 0.09	3.73± 0.19	2.06± 0.02	5.10± 0.15
soybean	0.97± 0.01	1.72± 0.39	1.06± 0.11	1.95± 0.02
peanut	5.74± 0.05	8.82± 0.27	5.70 ±0.15	8.85± 0.08
Maize	0.86± 0.13	2.72 ±0.04	1.01± 0.12	1.22± 0.13

Table 4. P-anisidine values (±standard deviations) of the olive oil and seed oil samples before and after high pressure treatment at 700 Mpa for 10 minutes at room temperature. The values were determined immediately after the treatment (T=0) and after 1 year of storage at 18° C (T=1 year)

Samples	P-anisidine			
	Raw T=0	Raw T=1 year	HP T=0	HP T=1 year
Olive oils				
A	1.65±0.01	0.70±0.24	3.87± 0.37	3.16± 0.26
B	4.66± 0.33	4.57± 0.89	4.67± 0.25	3.78± 0.61
C	1.69± 0.1	3.56± 0.14	2.45± 0.11	2.06± 0.75
D	2.07± 0.27	6.23± 0.96	3.07± 0.13	2.06± 0.5
E	5.21± 0.32	3.30± 0.34	3.68± 0.32	1.44± 0.82
F	6.59± 0.54	5.48± 0.46	5.97± 0.2	3.98 ±0.74
Seed Oils				
grape-stone	6.00± 0.2	8.37± 2.07	5.40± 0.18	8.98± 0.02
sunflower	1.08± 0.15	4.18± 1.13	3.02± 0.11	3.69± 0.57
soybean	2.43±0.21	4.19±0.37	1.13± 0.02	1.99± 0.23
peanut	0.83± 0.03	4.39± 0.5	3.18± 0.38	4.45± 0.45
Maize	0.58± 0.04	2.78± 0.43	0.86± 0.01	3.91± 0.62

Table 5. Peroxide values and p-anisidine values of soybean oil heat-treated at 120 °C for 10 minutes and soybean oil high pressure treated (700 MPa) for 10 minutes at room temperature. The values are compared to those of the untreated (T=0) samples.

Samples	Treatment time (min)	Peroxide value (mEq O_2/kg oil	p-anisidine	volatile hydrocarbons (total area)
Soybean oil heat treated	Time 0	0.97± 0.01	2.43 ±0.13	0
	after 10'	1.50± 0.04	3.78± 0.09	120±10
Soybean oils high pressure treated	Time 0	0.97± 0.01	2.43±0.13	0
	after 10'	1.06± 0.11	1.13±0.42	0

CANTARELLI (1969) for the extraction and that of GUTFINGER (1981) for the determinations.

- Total tocopherols by the HPLC, IUPAC method no 2.432 (1988).
- Fatty acids by capilllary GLC, Using the EFC method (1991) for olive oil analysis.

Table 1 reports some chemical characteristics of the seed oil samples, as described on their packing.

Results and Discussion

The saturated/unsaturated fatty acid ratio, phenolics and tocopherols of the olive oil samples supplied by the "Consorzio Producttori Olive del Triveneto" are reported in **table 2**.

The peroxide values (POV) of the raw and treated olive oil samples (**table 3**) did not show noticeable differences due to high pressure treatment in terms of primary oxidation products. The results concerning the seed oil samples showed that the high pressure treatment produced a more evident increase for the sunflower and grape-stone oil sample. Anyway these two seed oils had the highest levels of unsaturated fatty acids, which, as is known, affects lipid oxidation. The peroxide values of raw olive oils do not seem to be influenced by high pressure treatment in all cases; this is also true after 1 year of storage at -18 o C. Concerning the seed oil samples, the peroxide values either increased due to the high pressure treatment or as a result of the storage time.

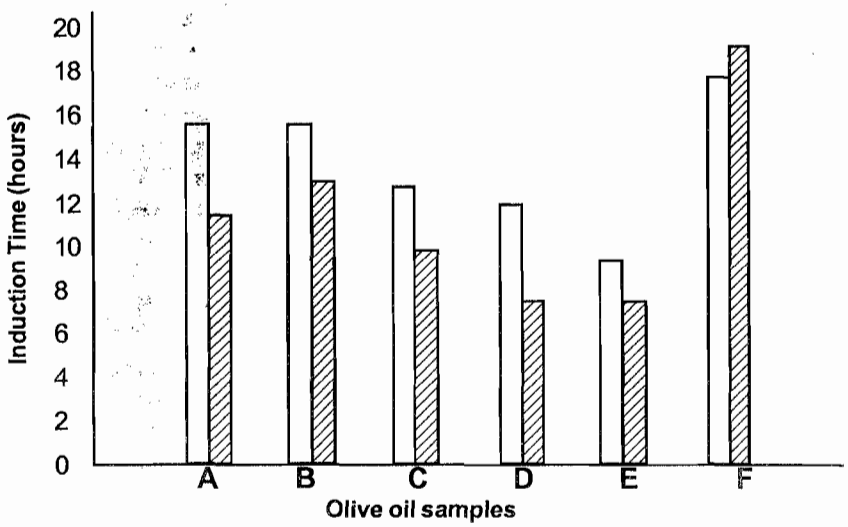

Fig. 1- Induction time of olive oil samples before (raw) and after (HP) high pressure treatment at 700 MPa for 10 minutes at room temperature

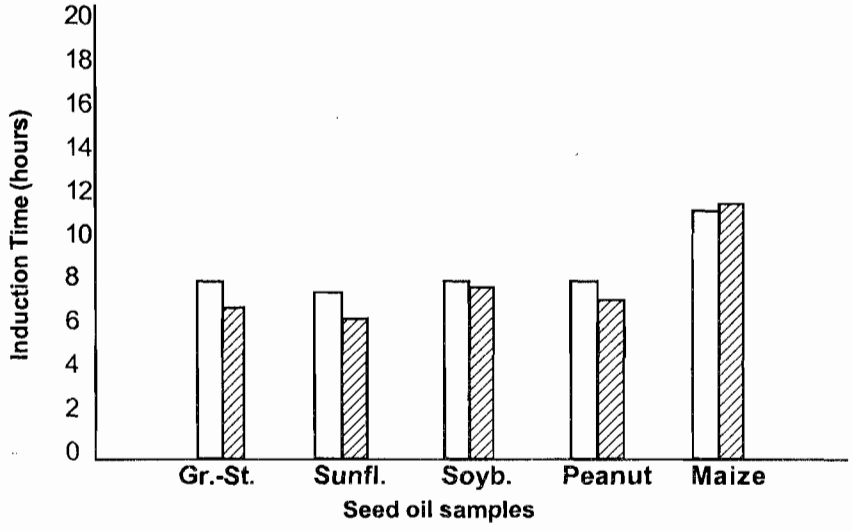

Fig. 2- Induction time of seed oil samples before (raw) and after (HP) high pressure treatment at 700 MPa for 10 minutes at room temperature

The para-anisidine value was used for the determination of the secondary oxidation products with a carbonylic functional group, such as aldehydes. **Table 4** reports the p-anisidine values of the raw and treated oil samples. Except for olive oil samples E and F, grape-stone and soybean oil samples, the p-anisidine index increased after the pressure treatment at time zero of storage. In particular, the peanut oil sample showed a decrease in the peroxide value and an increase in the p-anisidine value; this might be a typical effect of lipid oxidation. After 1 year of storage at -18° C, the AV of olive oils decreased in all samples except in the raw samples of C and D, whereas the values of the seed oils increased in all cases.

According to LOLIGER (1990), the volatile hydrocarbons may be considered a useful index to determine the secondary oxidation of oil. Head space vapour gas-chromatographic analysis was used to verify the probable presence of unacceptable flavours produced by treated oils. From the analyses, carried out with the vials maintained at 40° C, it was found that no detectable volatile hydrocarbons were in the head space of either the raw of the treated samples. On the contrary, heat treated oil samples (from pre-cooked foods stored at room temperature for two months), analysed at the same gas-chromatographic conditions, showed an increase of C1-C6 content in the head space vapour (LOLIGER, 1990). The hypothesis that the hydrocarbons were adsorbed by the container material can be considered unlikely because of the very brief contact time between the oil and containers (10 min treatment time). In fact, after the high pressure treatment, the oil samples were immediately placed in vials, equilibrated and analysed.

In **table 5** a comparison between soybean oil heat treated and soybean oil high pressure treated is presented in order to evaluate the effects of the two different processed in terms of peroxide value, p-anisidine value and volatile hydrocarbons present in the head space vapour of the samples. The heat treatment led to an increase in the secondary products of lipid oxidation, particularly.

In order to study the oxidative stability of the samples, the Rancimat test was carried out as an accelerated storage test

(HADORN and ZEURCHER, 1974, LERCKER et al., 1994). The induction time (length of the initial stage of very slow oxidation) of the treated olive oils was always shorter than that needed for the analogous raw, samples, except for oil F (commercial sample) (**fig. 1**). In seed oils (**fig. 2**), the grape-stone, sunflower and peanut oils showed a similar behaviour to the olive oils. In particular, the grape-stone and sunflower oil samples were the least resistant to oxidation, probably because of their unfavourale chemical composition (very low saturated to unsaturated fatty acid ratio). On the contrary, the soybean and maize oil samples showed, after hyperbaric treatment, a greater oxidative stability probably due to the high quality of the added tocopherols as antioxidants (table 1).

The different behaviour, in terms of induction time, of the commercial sample (F) in comparison to the other olive oils, is probably due to the different length of storage time of the samples. In fact, the A-E olive oil samples were produced 1 year before and underwent occasional contact with air and light.

Conclusions

From this preliminary investigation concerning the oxidative stability of oils after hyperbaric treatment, it is possible to observe that high pressure technology produced changes in the p-anisidine values of the oils, but not in the peroxide values and volatile hydrocarbons. with regard to the Rancimat test, the olive samples were, as expected, in all cases more resistant to oxidation than the seed oil samples. A comparison between high pressure and heat treatment, carried out on soybean oil samples, showed that the effect of heat treatment was more evident in terms of secondary lipid oxidation products (AV and volatile C1-C6). These results confirm those reported by KOWALSKY et al., (1996) regarding linolenic acid oxidation after high pressure treatment. In fact, according to their conclusions, a treatment above 600 Mpa suppresses autoxidation of linolenic acid. From the results of this study it is possible to conclude that, in order to prolong the shelf life of complex foods, containing lipidic fraction (pre-cooked foods, condiments etc.), it is advisable to use extra virgin olive oil instead of seed oil, when using high pressure technology. Moreover, it is necessary to take into consideration that the effects of high pressure treatment on oils was found to be dependent on origin, composition, initial quality and age of the oil.

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