

# Evaluation of the State of Oxidation of Crude Olive-Pomace Oils. Influence of Olive-Pomace Drying and Oil Extraction with Solvent

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The aim of this investigation was to follow the progress of oxidation during the phases of the industrial process of olive-pomace drying and the subsequent step of crude pomace oil extraction with solvent. Silica-gel column chromatography and high-performance size-exclusion chromatography were the analytical techniques utilized to this purpose. The data obtained showed that most of the oxidation occurs during industrial drying of the pomace with a mean increase of 35% in the oxidized triglycerides while no statistically significant increase was observed for triglyceride oligopolymers. The subsequent extraction of oil with solvent and the removal of the last traces of commercial hexane for the preparation of crude olive-pomace oil did not seem to entail any substantial increase in oxidation. There was a change in the state of oxidation given that there was an increase in triglyceride oligopolymers, which on average reached 0.32%, and in secondary oxidation products (mean *p*-anisidine value = 15.31). Hydrolytic degradation of crude pomace oils was particularly high with a mean value of free fatty acids of 9.24% and of diglycerides of 5.75%.

**Keywords:** *Triglyceride oligopolymers; oxidized triglycerides; partial glycerides; olive pomace; crude pomace oil*

## INTRODUCTION

Olive pomace is a byproduct of virgin olive oil processing (Firestone et al., 1988) which is of varying importance to all the countries of the Mediterranean basin where olives (*Oleaceae, Olea europaea*) are grown.

Oil may be extracted from olives either by means of conventional systems using hydraulic presses or by resorting to modern horizontal axis centrifuges. Both systems produce olive pomaces with differing percent rates of moisture: about 25% for the press-processed pomace and approximately 50% with the more recent machines (De Felice et al., 1979).

In Italy the use of centrifuges has currently become so widespread that only about 20% of the 568 000 t of olive pomace produced each year actually come from traditional processing plants (De Gennaro, 1996). This shift in choice is mainly predicated upon the fact that the centrifuges are labor-saving and allow continuous processing of the product although the olive pomace obtained is considerably moister and is thus more power-consuming to dry.

The residual oil is extracted from dried olive pomace by means of commercial hexane. The crude oil extracted then undergoes intensive refining to produce refined olive-pomace oil, which is finally mixed with virgin olive oil and is thus eligible for the commercial class of olive-pomace oil as defined by European Community (EC) regulation No. 356/92 (*Off. J. Eur. Communities*, 1992).

The olive pomace is dried with hot air at about 260 °C flowing through inside-bladed rotating cylinders. The substantial rise in the temperature may enhance the degree of oxidation of the oil the pomaces contain.

There are very few reports on this topic in the literature (Gomes, 1985, 1986). In particular, little is known about the extent of thermal damage caused by the drying process or about the influence of solvent

removal after oil extraction. The purpose of this investigation was to acquire experimental data providing greater insight into what changes occur in the oil subsequent to the processes of both drying and extraction.

## MATERIALS AND METHODS

The test samples were collected at the end of January 1995 at numerous pomace-processing plants situated in the province of Bari, in southern Italy.

Seven representative samples of approximately 3 kg each were collected from large stocks of moist pomace and another seven from corresponding industrially dried pomace. The moist olive-pomace samples were vacuum-dried at 30 °C in a stove in the laboratory to reach a residual moisture of about 5%. At the industrial processing plants the olive pomace had been dried in rotary dryers (Bernardini, 1982a; Hoffman, 1989). Drying occurred under the evaporating action of hot fumes coming from a depleted olive-pomace burner concurrently. Drying could be achieved to different degrees by changing the inflow of pomace. The temperature of the inflowing fumes was approximately 260 °C while temperatures ranged from 70 to 90 °C for the outflowing fumes.

The olive-pomace samples that had been vacuum-dried in the laboratory were then compared to the corresponding olive-pomace samples dried at the industrial processing plants to assess the extent of oxidation.

Oil extraction from the olive pomaces was effected in the laboratory with the following procedure: 1 L of *n*-hexane was added to 0.5 kg of olive pomace and left to mix for 15 min; the solvent-and-oil solution was separated, and then the process was repeated twice with 0.5 L of *n*-hexane. Finally the whole solution was filtered and the solvent removed under vacuum at a temperature of 30 °C by means of a rotating evaporator. Fourteen representative samples were also collected from large stocks of crude olive-pomace oil at several olive pomace-processing plants to determine the level of oxidative and hydrolytic degradation present. In the industrial plants the oil contained in dried olive pomaces was removed in stationary extractors with batch solvent. The dried olive pomace was conveyed to the extractors, where it was subjected to a solvent wash at a temperature of 35–40 °C. Washing was performed in series and in a countercurrent fashion (Bernardini, 1982b).

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**Table 1. Characteristics of the Olive Pomaces Tested**

olive pomace	moisture (%)	fat (%)	moisture after drying (%)	
			L <sup>a</sup>	I <sup>a</sup>
1	55.07	5.36	5.20	7.27
2	52.75	3.07	4.21	4.24
3	54.96	3.58	4.52	10.37
4	54.34	3.80	3.43	5.11
5	51.97	3.92	3.51	12.18
6	52.05	3.89	3.77	4.21
7	53.99	4.23	4.79	5.76

<sup>a</sup> L = laboratory; I = industry.

All the pomace oil samples underwent routine analyses for a first characterization, i.e., determination of the percent free fatty acids (FFA), peroxide values (PV), specific absorption at 232 nm ( $K_{232}$ ) (Off. J. Eur. Communities, 1991), and measurement of the *p*-anisidine value (*p*-AV) (IUPAC, 1987a). Polar compounds (PC) were separated and determined in each sample by means of silica-gel column chromatography as described by the IUPAC method (IUPAC, 1987b). The efficacy of column separation was checked by thin-layer chromatography. PCs in CH<sub>2</sub>Cl<sub>2</sub> were then submitted to high-performance size-exclusion chromatography (HPSEC) to quantify triglyceride oligopolymers, oxidized triglycerides, and partial glycerides. The HPSEC system consisted of a Perkin-Elmer series 10 pump, a 7125 S sample injector (rheodyne), a 50  $\mu$ L injector loop, a PL-GEL guard column (Perkin-Elmer Ltd., Beaconsfield, Great Britain) of 7.5 mm i.d.  $\times$  5 cm length, and a series of three PL-GEL columns (Perkin-Elmer Ltd., Beaconsfield, Great Britain) of 7.5 mm i.d.  $\times$  30 cm length. The three columns were packed with 5  $\mu$ m particles having pore diameters of 500, 500, and 100  $\text{\AA}$ , respectively. The detector was a differential refractometer connected to an integrator. The elution solvent used was CH<sub>2</sub>Cl<sub>2</sub> for HPLC at a flow rate of 1 mL/min.

The procedures for identifying the peaks on the chromatograms and for the quantitative assessment of the relevant compounds of interest have already been described in a previous paper (Gomes, 1992). The data from the different sample sets were compared by means of the one-way analysis of variance (ANOVA) followed by Duncan's multiple-range test.

## RESULTS AND DISCUSSION

Table 1 shows the characteristics of the olive pomaces examined. As may be evinced considering the moisture rates, these were pomaces produced at oil mills where continuous olive-oil extraction systems are utilized. The moisture rates ranged from 3.43 to 5.20% for olive pomaces dried in the laboratory and from 4.21 to 12.18% for pomaces subjected to an industrial scale drying process. Table 2 refers to the levels of oxidation and reports the differences between the oils extracted from olive pomaces which had been dried in the laboratory and the oils obtained from the same olive pomace which had been subjected to an industrial scale drying process.

All the routine parameters measured to determine the level of oxidation increased notably in each sample. In particular, the mean levels of PV rose from 18 to 28.4 with a 57% increase,  $K_{232}$  from 3.012 to 3.462 with a 14% increase, and *p*-AV from 10.29 to 11.28 with about a 10% increase, thus indicating that considerable changes occur with both primary and secondary oxidation products.

Determination of oxidized triglycerides and oligopolymers by means of HPSEC of PCs provided further important information. In particular, by estimating all the forms of triglyceride oxidation, oxidized triglycerides provide a more direct and appropriate measurement of the state of oxidation. Table 2 also shows that the mean values of oxidized triglycerides rose from 1.99 to 2.69% with a 35% increase, thus once again pointing to the substantial degradation which occurs when olive pomaces undergo industrial scale drying processes. The triglyceride dimers increased slightly with mean values moving on from 0.21% to 0.26% except for sample 5, where they remained unchanged. These figures are, however, very low and may be due to the high level of oxidation. Indeed, the theory on fatty substance oxidation admits that dimers may be formed (Gomes, 1995).

Previous papers have reported that vegetable oil refining results in the presence of oligopolymeric substances mainly due to the high temperatures reached during deodorization (Hopia, 1993). The fact that oligopolymers do not increase during drying despite the high temperature of the air is ascribable to the high moisture rate of olive pomaces, which actually exposes them to much lower temperatures. The statistical analyses showed that, though on average the PV increased, the variations were not significant. This was also the case for the triglyceride oligopolymers mainly due to the very slight differences observed, and for the *p*-AV. By contrast, significant variations were detected for both oxidized triglycerides ( $p < 0.05$ ) and  $K_{232}$  ( $p < 0.01$ ), and this showed that the determination of these two parameters is particularly useful to track oxidative deterioration. Hence, on the basis of the data obtained, industrial scale pomace-drying processes may be said to unquestionably enhance oxidation of the oil in the olive pomace without having any patent influence on the formation of triglyceride polymerization products.

Fourteen representative samples were collected from large stocks of crude olive-pomace oil at several pomace-processing plants and then analyzed to gather information on the oxidation levels of olive-pomace oils after extraction with solvent. The data obtained are shown in Table 3. The PCs comprised substances with a greater polarity than the unchanged triglycerides and mainly consisted of fatty acids and partial glycerides

**Table 2. Oxidation Levels in Oils Extracted from Olive Pomaces Dried by Laboratory and by Industrial Scale Processes**

olive pomace	PV		$K_{232}$		<i>p</i> -AV		oxidized triglycerides (%)		triglyceride dimers (%)	
	L <sup>a</sup>	I <sup>a</sup>	L	I	L	I	L	I	L	I
1	16.2	19.1	2.746	3.315	8.80	10.55	1.49	1.67	0.24	0.27
2	16.3	27.5	3.062	3.364	11.43	12.15	1.84	2.57	0.22	0.26
3	18.5	27.3	3.092	3.486	10.51	11.57	1.20	2.07	0.18	0.25
4	24.1	26.9	2.488	3.618	9.54	10.09	2.44	2.91	0.18	0.20
5	16.9	39.3	3.530	3.872	13.23	14.12	1.99	3.00	0.32	0.32
6	13.5	24.3	2.685	2.724	9.82	10.79	2.31	3.32	0.14	0.25
7	20.8	39.4	3.555	3.859	8.74	9.67	2.66	3.29	0.25	0.31
min	13.5	19.1	2.488	2.724	8.74	9.67	1.20	1.67	0.14	0.20
max	24.1	39.4	3.555	3.872	13.23	14.12	2.66	3.32	0.32	0.32
mean	18.0	28.4	3.022	3.462	10.29	11.28	1.99	2.69	0.22	0.26
SD ( $n - 1$ )	3.5	8.0	0.410	0.394	1.60	1.51	0.52	0.62	0.06	0.04

<sup>a</sup> L = laboratory pomace drying and oil extraction. I = industrial scale pomace drying and laboratory oil extraction.

**Table 3. Characteristics of Crude Olive-Pomace Oil (Industrial Scale Processing)**

olive pomace	polar compounds (%)	FFA (% oleic acid)	diglycerides (%)	PV (mequiv/kg)	$K_{232}$	<i>p</i> -AV	oxidized triglycerides (%)	triglyceride dimers (%)
1	15.23	6.28	4.69	35.0	4.278	10.38	3.21	0.50
2	17.38	8.10	5.37	35.5	4.500	13.36	2.61	0.23
3	16.79	7.28	5.83	28.8	4.116	9.17	2.66	0.25
4	18.88	9.21	5.05	38.8	5.472	18.85	3.65	0.26
5	20.42	11.56	5.42	32.4	4.891	16.66	2.42	0.34
6	14.08	6.52	4.30	14.3	3.884	12.21	2.48	0.28
7	19.25	11.34	5.08	12.7	4.467	16.47	1.90	0.34
8	16.55	8.16	5.08	10.6	4.292	17.00	2.25	0.29
9	18.27	10.88	4.61	11.0	4.575	17.39	1.85	0.26
10	18.18	8.06	7.25	15.0	4.476	17.44	2.00	0.45
11	16.28	7.35	6.15	12.8	4.367	15.56	2.17	0.20
12	28.35	14.09	9.77	14.9	4.900	16.36	2.79	0.32
13	17.68	9.17	5.15	12.7	4.551	19.69	2.45	0.30
14	20.40	11.33	6.70	15.2	4.545	14.70	1.91	0.48
min	14.08	6.52	4.30	10.6	3.884	9.17	1.85	0.20
max	28.35	14.09	7.25	38.8	5.472	19.69	3.65	0.50
mean	18.41	9.24	5.75	20.3	4.522	15.31	2.45	0.32
SD ( <i>n</i> - 1)	3.38	2.28	1.41	10.4	0.382	3.04	0.51	0.09

**Table 4. Differences in Oxidation Levels during Crude Olive-Pomace Oil Production**

determination	ANOVA	sample sets <sup>a</sup>		
		1	2	3
triglyceride dimers	<i>p</i> < 0.05	0.22 ± 0.06 <sup>a</sup>	0.26 ± 0.04 <sup>a,b</sup>	0.32 ± 0.09 <sup>b</sup>
oxidized triglycerides	<i>p</i> < 0.05	1.99 ± 0.52 <sup>a</sup>	2.69 ± 0.62 <sup>b</sup>	2.45 ± 0.51 <sup>a,b</sup>
<i>p</i> -AV	<i>p</i> < 0.01	10.29 ± 1.60 <sup>a</sup>	11.28 ± 1.51 <sup>a</sup>	15.31 ± 3.04 <sup>b</sup>
PV	ns <sup>b</sup>	18.0 ± 3.5 <sup>a</sup>	28.4 ± 8.0 <sup>a</sup>	20.3 ± 10.4 <sup>a</sup>
$K_{232}$	<i>p</i> < 0.05	3.022 ± 0.410 <sup>a</sup>	3.462 ± 0.394 <sup>b</sup>	4.522 ± 0.382 <sup>c</sup>

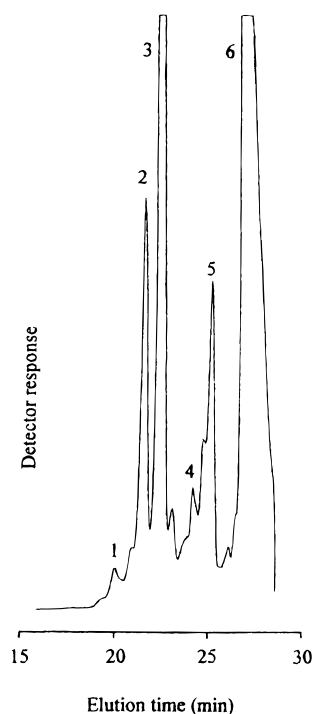
<sup>a</sup> Mean ± SD. One common reading indicates no significance. 1 = laboratory olive-pomace drying and oil extraction. 2 = industrial scale olive-pomace drying and laboratory oil extraction. 3 = industrial scale olive-pomace drying and oil extraction. <sup>b</sup> Not significant.

as well as oxidized triglycerides and oligopolymeric substances. PCs thus provided an overall indication of hydrolytic and oxidative degradation. The values measured were very high (range = 14.08–28.35, mean = 18.41%, SD = 3.38) mainly because of the great amounts of free fatty acids and partial glycerides present. This can be evinced in Figure 1 which depicts the HPSEC chromatogram of the PCs of a crude olive-pomace oil.

The same figure also indicates that we were able to separate free sterols and triterpene diols from the fatty acids by resorting to the analytical technique we had developed and thus improved on the chromatographic separations obtained up to then (Gomes and Caponio, 1996). This meant that we were able to collect more data to characterize the sample. The method developed is particularly versatile as it provides quantitative information on oligopolymers, oxidized triglycerides, partial glycerides, sterols and triterpene diols, and fatty acids with only one analysis. Furthermore, it is sensitive enough to pick up the small amounts of oligopolymers observed.

Examination of the differences between the oils extracted in the laboratory from industrially dried olive pomaces and the pomace oils extracted with solvent at the industrial processing plants showed that the PV was lower on average in the industrial processing plant oils (mean value = 20.3 versus 28.4) though this result was countered by a higher mean value of *p*-AV (mean value = 15.31 versus 11.28). On average, greater values of  $K_{232}$  (mean value = 4.522 versus 3.462) and of triglyceride dimers (mean value = 0.32% versus 0.26%) were also found in the industrially produced crude olive-pomace oils. Conversely, oxidized triglycerides remained virtually unchanged at an average of 2.45%. Finally, the diglycerides amounted to 5.75% on average (range = 4.30–7.25, SD = 1.41), which pointed to the extreme hydrolytic degradation of oils.

Statistically, the variations in *p*-AV and  $K_{232}$  were



**Figure 1.** HPSEC of polar compounds in crude olive-pomace oil: (1) triglyceride dimers, (2) oxidized triglycerides, (3) diglycerides, (4) monoglycerides, (5) free sterols and triterpene diols, (6) free fatty acids.

significant while the increase in oligopolymers was too scanty to be significant. Even in this case, as before, the PV did not appear to be significantly different considering the broad, partially superimposable ranges containing the experimental data. The results of the statistical analyses on all sets of samples examined are reported in Table 4. Clear-cut differences were found in the oligopolymer contents of oils extracted in the

laboratory from olive pomaces dried in the laboratory, too, as compared to the oils extracted at the industrial processing plants from industrially dried olive pomaces. Hence industrial scale processes, on the whole, led to an increase in the oligopolymers as the values observed, albeit low, increased by 45%. This phenomenon may be accounted for by considering the global effect produced by the industrial scale drying process and by the introduction of superheated steam into the oil to remove the solvent remnants.

The only difference in oxidized triglycerides was found between the first and second series of samples and corresponded to the different drying processes utilized, thus indicating that most of the oxidation occurs during this phase.

A statistical difference was consistently found for  $K_{232}$  ( $p < 0.05$ ) but not for PV, which is thus unsuitable for measuring the level of oxidation of the lipid fraction during the industrial scale process for the production of crude olive-pomace oil. Finally, there was a clear-cut difference between the  $p$ -AVs of the first and third sets of samples and between the second and third. The substantial increase in the  $p$ -AVs in the third set of samples may be ascribed to the partial degradation of hydroperoxides and the formation of secondary oxidation products.

#### CONCLUSION

The experimental data obtained suggest that most of the oxidation process occurs during pomace drying with significantly higher values of  $K_{232}$  and oxidized triglycerides, the latter increasing by 35%. Subsequent oil extraction with solvents does not seem to entail any substantial increase in oxidation. What does seem to take place is a change in the state of oxidation as documented by the increase in oligopolymers, which, however, remain low, and in secondary oxidation products. Oxidized triglycerides remain virtually unchanged.

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Received for review August 9, 1996. Accepted January 14, 1997.\*

JF960603N

\* Abstract published in *Advance ACS Abstracts*, March 1, 1997.