# Oxidative Stability of Virgin Olive Oils

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**ABSTRACT:** An investigation was carried out on virgin olive oils of the Gentile (Larino), Gentile (Colletorto), Coratina, and Leccino varieties, harvested at different times, to assess their oxidation stability. The olive oils were analyzed by means of peroxide, $K_{232}$, and $K_{270}$ values at 1, 6, 12, and 18 mon of storage in green bottles, in the dark, at temperatures ranging from a mean of 6°C in winter to 12°C in summer. A subsample was also oven-tested at 75°C and then analyzed on a weekly basis using the same oxidative parameters. The less ripe the olives (harvested in the same area during 1 mon), the more resistant the olive oils were to forced oxidation. The amount of total phenols in the oils was found to be directly related, even if to a low degree, to the oleuropein content in the olives and inversely related, to the same degree, to (3,4-dihydroxyphenyl)ethanol. The latter is a derivative of oleuropein; (3,4-dihydroxyphenyl)ethanol content increases as the olives ripen, but it is very low in fresh virgin olive oils, owing to the hydrophilic nature of the phenolic alcohol, which goes mainly into the wastewater during processing. Among the varieties considered, Coratina oils showed the highest resistance to forced oxidation because of their high total phenol content.

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**KEY WORDS:** (3,4-Dihydroxyphenyl)ethanol, $K_{232}$, $K_{270}$, oleuropein, olive variety, peroxide value, phenolic compounds, thermal oxidation, virgin olive oil.

Virgin olive oils are known to be more resistant to oxidation than other edible oils because of their content of natural antioxidants and lower unsaturation levels; the higher the number of double bonds in fatty acids, the shorter is the induction period for oil autoxidation, the main cause of their alteration. The stability of virgin olive oils is due to their natural phenolic compounds, since these compounds are able to donate a hydrogen atom to the lipid radical formed during the propagation phase of lipid oxidation (1). Oleuropein, a glycosidic ester of elenolic acid, and (3,4-dihydroxyphenyl)ethanol (3,4-DHPEA = hydroxytyrosol), is the main phenolic compound in olives although it decreases notably during the course of ripening, and its content is negligible in the olive oils, where derivatives of oleuropein hydrolysis during extraction dominate. For instance, glycosidases catalyze the hydrolysis of oleuropein, with the production of oleuropein aglycon and the dialdehydic form of elenolic acid linked to 3,4-DHPEA. Nevertheless, the resistance to oxidation is mainly due to phenolic compounds arising from the glycated precursors, the most important of which is oleuropein, present in the olives before extraction. Therefore, the phenol content of virgin olive oils depends on the fruits' ripeness, variety, climatic conditions, and the oil extraction processes (2–6). Oxidative stability has been correlated to the total hydrophilic phenols, to the *ortho*-diphenol compounds (7,8) such as 3,4-DHPEA, which increases during olive maturation, and to the oleosidic forms of 3,4-DHPEA (9). The antioxidant activity of α-tocopherol has been evaluated in olive oils and model systems (10). For instance, the percentage contribution of the α-tocopherol to the oil's stability, as measured by Rancimat, was estimated to be less than that contributed by the composition of fatty acids (24%), and substantially less than that contributed by phenolic and orthodiphenolic compounds (51%) (11).

Very little is known about the relationship between the phenolic composition of olives during maturation, and the stability of the oils. In a previous work, the authors studied phenolic compounds in different olive varieties, taking into account the degree of ripeness of the drupes (12). The aim of this present research was to assess the resistance to oxidation of virgin olive oils, typical of the area studied, obtained from the above mentioned varieties, by evaluating the relationship between the phenolic compounds and the stability of the oils. This latter was analyzed by means of peroxide, $K_{232,}$ and $K_{270}$ values at 1, 6, 12, and 18 months of storage. Moreover, a subsample was also oven-tested at 75°C and then analyzed on a weekly basis using the same oxidative parameters.

## EXPERIMENTAL PROCEDURES

*Olive sampling and fruit analysis*. The samples consisted of olives (*Olea europea* L.) of the Gentile (Larino), Gentile (Colletorto), Coratina and Leccino varieties. [Gentile (Larino) and Gentile (Colletorto) are two distinctly different cultivars grown in the same province but under different soil and climate conditions.] The drupes were hand-picked at different stages of ripeness in the Molise region in November 1995 and stored in 25-kg plastic boxes for 24 h before processing. Sampling was limited to the period when the olives are usually harvested and processed in the area considered. An unambiguous "olive ripening index" to establish when to pick the drupes to obtain the best quality oils has not yet been devised; several that have been tried include the malic acid/citric acid ratio of drupes (13), the climacteric phase of olives (14), and/or the pigmentation or semipigmentation (the beginning of shift in skin color from green to purple) of drupes (15). In our study, the maturation index was determined according to the method proposed by the

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**TABLE 1**
**Maturation Index, Hunter Color Values (L*, a*, b*)[a], and Phenolic Compounds (mg/g)[b] of Olive Fruits at Different Harvest Times**

| Varieties | Harvest time | Identification | Maturation index[c] | L* | a* | b* | 3,4-DHPEA | Oleuropein |
|---|---|---|---|---|---|---|---|---|
| Leccino | 11/01/95 | LecI | 4.8 | 28.4 ± 3.4 | −2.1 ± 0.1 | 1.9 ± 0.12 | 0.37 ± 0.05 | 0.97 ± 0.11 |
| Leccino | 11/15/95 | LecII | 4.5 | 31.0 ± 3.7 | −1.8 ± 0.1 | 3.6 ± 0.29 | 0.60 ± 0.08 | 0.85 ± 0.09 |
| Leccino | 11/30/95 | LecIII | 4.9 | 27.2 ± 2.4 | −2.4 ± 0.2 | 5.1 ± 0.3 | 0.72 ± 0.06 | 0.72 ± 0.08 |
| Gentile (Larino) | 11/01/95 | GeLI | 2.2 | 44.0 ± 3.2 | −3.1 ± 0.2 | 12.2 ± 0.9 | 0.15 ± 0.03 | 1.12 ± 0.15 |
| Gentile (Larino) | 11/15/95 | GeLII | 2.6 | 42.7 ± 5.2 | −6.5 ± 0.4 | 17.3 ± 1.5 | 0.48 ± 0.05 | 1.45 ± 0.19 |
| Gentile (Larino) | 11/30/95 | GeLIII | 3.9 | 38.1 ± 3.8 | −1.8 ± 0.3 | 9.8 ± 0.8 | 0.62 ± 0.08 | 0.87 ± 0.09 |
| Coratina | 11/01/95 | CorI | 0.4 | 52.0 ± 4.8 | −14.4 ± 0.9 | 24.7 ± 2.6 | 0.30 ± 0.06 | 1.44 ± 0.21 |
| Coratina | 11/15/95 | CorII | 0.8 | 53.6 ± 3.5 | −19.5 ± 1.2 | 27.6 ± 2.2 | 0.47 ± 0.07 | 1.62 ± 0.18 |
| Coratina | 11/30/95 | CorIII | 0.7 | 48.8 ± 4.2 | −17.6 ± 1.5 | 26.9 ± 2.5 | 0.52 ± 0.06 | 1.21 ± 0.16 |
| Gentile (Colletorto) | 11/01/95 | GeCI | 4.2 | 32.7 ± 4.3 | 1.0 ± 0.1 | −0.1 ± 0.02 | 0.40 ± 0.07 | 2.08 ± 0.29 |
| Gentile (Colletorto) | 11/15/95 | GeCII | 4.9 | 29.3 ± 4.0 | −0.5 ± 0.04 | 2.7 ± 0.16 | 0.97 ± 0.12 | 1.91 ± 0.21 |
| Gentile (Colletorto) | 11/30/95 | GeCIII | 4.8 | 30.7 ± 2.9 | −3.8 ± 0.4 | 2.3 ± 0.28 | 1.10 ± 0.15 | 1.50 ± 0.19 |

[a]Means ± standard deviations (SD) of 20 determinations.
[b]Means ± SD of three determinations. 3,4-DHPEA, (3,4-dihydroxyphenyl)ethanol, also known as hydroxytyrosol.
[c]Determined by the Jaèn index.

National Institute of Agronomic Research of Spain (San Jaén Station), which in brief consists of distributing randomly taken samples of 100 olives in eight groups according to skin color. Maturation index values range from 0 (bright green) to 7 (purple) (16). Moreover, a colorimeter (CR-200b Chromometer, Minolta, Japan) was used to assess the color of 20 fruit samples to which the Hunter colorimetric system was applied (L*, lightness; a*, redness; b*, yellowness). Detection and quantification of phenolic compounds were carried out by HPLC analysis (12).

*Olive sample processing*. The virgin olive oil samples were obtained by industrial processing; about 200 kg of olives from the Gentile (Larino), Gentile (Colletorto), Coratina, and Leccino varieties were milled for 30 min with a four-stone mill, kneaded for 12 min at 20–22°C, and subjected to pressure extraction. The oil samples (for identification, see Table 1) were not filtered, and their average level of humidity was about 0.2% (w/w). The samples were stored for 18 mon in green bottles in a dark storeroom at a mean temperature that ranged from 6°C in winter to 12°C in summer.

*Reagents and standards*. HPLC or analytical-grade reagents and solvents were supplied by Carlo Erba (Milano, Italy). Gallic acid, (*p*-hydroxyphenyl)ethanol (*p*-HPEA), and α-tocopherol were produced by Fluka (Buchs, Switzerland); oleuropein was purchased from Extrasinthèse (Z.I. Lyon-Nord, Genay, France).

*Oil sample analysis*. The following parameters were determined within 1 mon: free fatty acids, peroxide values (PV), spectrophotometric properties, fatty acids, methyl esters (17), α-tocopherol (18), and total phenols at 765 nm, using the Folin-Ciocalteau reagent on a water/methanolic extract of the oils, and expressed as gallic acid. The polar fraction extract (19) was evaporated to dryness in a rotary evaporator at 40°C, and the residue was dissolved in methanol. Detection and quantification were carried out by HPLC in a Waters 600 apparatus (Milford, MA) with a photodiode array detector (Waters 991). The 250 × 4 mm column used was filled with Supelcosil ABZ + Plus (Supelco Inc., Bellefonte PA) and the flow rate was 1.3 mL $min^{-1}$. The volume of injection was 20 μL. The eluates were detected by means of a photodiode array at 280 nm (a wavelength at which phenolic compounds typically absorb) and 25°C. The mobile phase used was 2% acetic acid in water (W) and methanol (M) for a total running time of 50 min, using the following gradients: from 97%W-3%M to 80%W-20%M in 10 min, 60%W-40%M in 10 min, 45%W-55%M in 15 min; and 0%W-100%M in 5 min until the end of the run.

The quantification of *p*-HPEA was carried out using the external standard method, and the response factor of *p*-HPEA was used to quantify the 3,4-DHPEA. The identification of 3,4-DHPEA was carried out on the basis of the GC–MS spectrum recorded (20). The phenolic compounds also were analyzed after 6, 12, and 18 mon of storage.

*Oven testing*. The thermal oxidation process was carried out on subsamples of oil taken from each sample after 6 mon of storage. The oil samples, 0.250 L, contained in open bottles, were subjected to oven testing in a static oven at the standard temperature of 75 ± 1°C for the Schaal oven test. During oven testing, the PV, $K_{232}$, and $K_{270}$ values were monitored on a weekly basis until they reached 70 meq of active oxygen per kg of olive oils.

*Statistical analysis*. After confirming that they were within the norm, the data were analyzed using the StatView SE software program (Abacus Concepts, Inc., Berkeley, CA). To calculate the confidence intervals and to perform the hypothesis test for a paired test, a single sample analysis (using a paired samples procedure) was adopted. A linear regression analysis was carried out to evaluate the relationship between the PV, $K_{232}$, and $K_{270}$ values, and oven-testing periods.

## RESULTS AND DISCUSSION

The oils under study were obtained from several olive varieties picked at three harvest times. Their maturation index was inversely proportional to the lightness (L*), and yellowness (b*) values, and directly proportional to the redness (a*) value: mat-

**TABLE 2**
**Free Fatty Acids and Fatty Acid Composition (%) in 1-mon Virgin Olive Oils[a]**

| Samples | Free fatty acids (% oleic acid) | C16:0 | C16:1 | C18:0 | C18:1n-9 | C18:2n-6 | C18:3n-3 |
|---|---|---|---|---|---|---|---|
| LecI | 0.1 ± 0.06 | 12.7 ± 0.10 | 0.8 ± 0.10 | 1.9 ± 0.18 | 78.1 ± 1.23 | 5.0 ± 0.07 | 0.5 ± 0.07 |
| LecII | 0.2 ± 0.04 | 11.3 ± 0.10 | 0.7 ± 0.11 | 2.0 ± 0.15 | 78.4 ± 0.98 | 6.1 ± 0.11 | 0.6 ± 0.09 |
| LecIII | 0.2 ± 0.03 | 10.8 ± 0.09 | 1.0 ± 0.09 | 2.0 ± 0.12 | 78.7 ± 0.82 | 6.3 ± 0.24 | 0.4 ± 0.08 |
| GeLI | 0.3 ± 0.04 | 12.2 ± 0.22 | 1.1 ± 0.08 | 3.0 ± 0.12 | 72.5 ± 1.10 | 9.7 ± 0.31 | 0.7 ± 0.02 |
| GeLII | 0.3 ± 0.02 | 10.9 ± 0.51 | 0.7 ± 0.11 | 3.0 ± 0.12 | 76.5 ± 0.88 | 7.6 ± 0.22 | 0.5 ± 0.08 |
| GeLIII | 0.2 ± 0.03 | 10.5 ± 0.14 | 0.8 ± 0.09 | 2.0 ± 0.10 | 76.8 ± 1.03 | 8.1 ± 0.19 | 0.6 ± 0.05 |
| CorI | 0.3 ± 0.04 | 13.4 ± 0.28 | 0.8 ± 0.08 | 2.5 ± 0.14 | 73.9 ± 0.48 | 7.6 ± 0.22 | 0.7 ± 0.02 |
| CorII | 0.3 ± 0.02 | 10.3 ± 0.18 | 0.7 ± 0.10 | 2.3 ± 0.11 | 77.8 ± 0.77 | 6.9 ± 0.18 | 0.7 ± 0.06 |
| CorIII | 0.2 ± 0.03 | 9.9 ± 0.42 | 0.5 ± 0.12 | 2.4 ± 0.13 | 79.1 ± 0.91 | 6.5 ± 0.12 | 0.7 ± 0.08 |
| GeCI | 0.3 ± 0.02 | 16.5 ± 0.89 | 1.6 ± 0.14 | 2.5 ± 0.16 | 69.1 ± 0.74 | 9.0 ± 0.23 | 0.7 ± 0.04 |
| GeCII | 0.2 ± 0.03 | 15.4 ± 0.38 | 1.5 ± 0.10 | 1.6 ± 0.12 | 70.7 ± 0.98 | 9.3 ± 0.19 | 0.7 ± 0.04 |
| GeCIII | 0.3 ± 0.02 | 11.8 ± 0.31 | 1.3 ± 0.08 | 2.5 ± 0.15 | 74.8 ± 1.21 | 8.0 ± 0.15 | 0.6 ± 0.05 |

[a]Means and SD of three determinations. For sample codes and abbreviation see Table 1.

uration index vs. L* ($r = -0.98$, $P \leq 0.0001$), maturation index vs. b* ($r = -0.96$, $P \leq 0.0001$), maturation index vs. a* ($r = 0.89$, $P \leq 0.0001$). The highest values of lightness and yellowness and the lowest values of redness and of the maturation index were found in the Coratina olives, since the black maturation phase had not been reached in the harvest time considered (Table 1). The statistics on the acidic composition of the 1-mon olive oil samples are given in Table 2. The percentage content of the major fatty acids varied in relation to the variety and the harvest time of the olives: oleic acid content increased, whereas palmitic acid decreased with the growing maturity of the olives.

During 18 mon of storage in bottles filled to the brim with unfiltered oil and stored in a dark storeroom at low temperatures, the PV, $K_{232}$, and $K_{270}$ values of the oils increased slightly and were below the European Common Market limit for extra-virgin olive oil (Table 3). The oil stability did not vary significantly during storage in relation to the varieties and to the degree of ripeness.

In all 1-mon virgin olive oil samples, the riper the olives were, the lower the total phenol content was (20,21), ranging from 642 ppm in the Coratina I (CorI) to 101 ppm in the Leccino III (LecIII) oils (Table 4). The average complex phenolic fraction was over 90% of the total HPLC peak area, and the simple fraction was mainly represented by *p*-HPEA and 3,4-DHPEA, which ranged from less than 1 ppm of oil in Leccino II (LecII) and LecIII to about 47 ppm in Gentile Colletorto I (GeCI). A low concentration of 3,4-DHPEA was found in the fresh oils compared with the amounts in the olives, whose values, higher in the riper drupes, ranged from 0.15 mg/g of pulp in Gentile Larino I (GeLI) to 1.10 mg/g of pulp in Gentile Colletorto III (GeCIII) (Table 1). A negative correlation, although to a low degree, was found between the amount of 3,4-DHPEA in the olives and the total phenols in the oils ($r = -0.48$), while a positive correlation was found between the amount of oleuropein in the olives, decreasing during maturation, and the total phenols in the oils ($r = 0.49$). These results are attributable to the hydrophilic nature of the phenolic alcohol, which goes mainly into the wastewater during processing compared to the less polar complex phenols, which represent the phenolic reserve of fresh oils. Table 4 shows the reduction in total phenols after 6, 12, and 18 mon of storage—owing to oxidation and hydrolytic activities during storage—and the evolution of 3,4-DHPEA. The latter showed a typical rising trend after 6 mon of storage, followed by a falling trend caused by a

**TABLE 3**
**Peroxide Values (PV; meq $O_2$/kg), $K_{232}$, and $K_{270}$ Values in Virgin Olive Oils During Storage at 1 (a), 6 (b), 12 (c), and 18 (d) mon[a]**

| | PV | | | | $K_{232}$ | | | | $K_{270}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Samples | a | b | c | d | a | b | c | d | a | b | c | d |
| LecI | 2.7 | 6.2 | 6.6 | 10 | 1.5 | 1.5 | 1.6 | 1.7 | 0.14 | 0.16 | 0.16 | 0.19 |
| LecII | 3.3 | 4.1 | 5.5 | 6.1 | 1.6 | 1.4 | 1.5 | 1.6 | 0.12 | 0.10 | 0.16 | 0.18 |
| LecIII | 4.9 | 6.3 | 8.2 | 8.5 | 1.4 | 1.6 | 1.6 | 1.9 | 0.11 | 0.10 | 0.14 | 0.17 |
| GeLI | 3.1 | 4.2 | 6.3 | 6.6 | 1.5 | 1.6 | 1.6 | 1.6 | 0.14 | 0.15 | 0.16 | 0.19 |
| GeLII | 3.2 | 4.3 | 5.8 | 6.5 | 1.7 | 1.6 | 1.6 | 1.7 | 0.17 | 0.19 | 0.18 | 0.20 |
| GeLIII | 3.9 | 4.4 | 6.2 | 6.7 | 1.7 | 1.7 | 1.7 | 1.6 | 0.14 | 0.15 | 0.15 | 0.18 |
| CorI | 2.3 | 4.0 | 5.2 | 8.3 | 1.6 | 1.7 | 1.8 | 1.8 | 0.16 | 0.18 | 0.17 | 0.19 |
| CorII | 3.4 | 4.0 | 5.6 | 15 | 1.7 | 1.7 | 1.8 | 1.8 | 0.16 | 0.18 | 0.19 | 0.20 |
| CorIII | 2.5 | 4.2 | 6.3 | 13.8 | 1.7 | 1.9 | 1.8 | 1.8 | 0.13 | 0.14 | 0.15 | 0.18 |
| GeCI | 3.9 | 7.4 | 8.7 | 10.7 | 1.7 | 1.7 | 2.1 | 2.1 | 0.15 | 0.14 | 0.14 | 0.16 |
| GeCII | 4.1 | 5.9 | 7.1 | 10.7 | 1.8 | 1.8 | 1.9 | 1.9 | 0.15 | 0.14 | 0.19 | 0.19 |
| GeCIII | 3.3 | 4.3 | 4.8 | 14.2 | 1.9 | 1.7 | 2.1 | 2.1 | 0.18 | 0.19 | 0.20 | 0.20 |

[a]Means of three determinations; coefficient of variation was always <5%. For sample codes see Table 1.

**TABLE 4**
**Hydroxytyrosol (3,4-DHPEA) and Total Phenol Content (ppm of gallic acid) of Stored Virgin Olive Oils at 1, 6, 12, and 18 mon[a]**

| | 3,4-DHPEA | | | | Total | | | |
|---|---|---|---|---|---|---|---|---|
| Samples | 1 mon | 6 mon | 12 mon | 18 mon | 1 mon | 6 mon | 12 mon | 18 mon |
| LecI | 3.7 ± 0.18 | 38.4 ± 1.75 | 8.3 ± 0.02 | 10 ± 0.16 | 455 ± 32 | 241 ± 18 | 142 ± 8 | 140 ± 9 |
| LecII | 0.2 ± 0.01 | 2.5 ± 0.01 | 0.0 | 2.1 ± 0.04 | 133 ± 11 | 94 ± 5 | 71 ± 3 | 41 ± 2 |
| LecIII | 0.1 ± 0.02 | 3.6 ± 0.05 | 0.0 | 13.2 ± 0.12 | 101 ± 6 | 83 ± 7 | 61 ± 3 | 40 ± 3 |
| GeLI | 6.3 ± 0.21 | 8.6 ± 0.35 | 6.1 ± 0.09 | 17.2 ± 1.65 | 411 ± 31 | 200 ± 16 | 132 ± 7 | 124 ± 5 |
| GeLII | 6.5 ± 0.88 | 21.6 ± 1.1 | 26.7 ± 0.11 | 16.4 ± 0.98 | 427 ± 38 | 230 ± 12 | 110 ± 6 | 108 ± 4 |
| GeLIII | 4.2 ± 0.06 | 1.8 ± 0.02 | 17.8 ± 083 | 20.0 ± 0.95 | 323 ± 22 | 174 ± 6 | 102 ± 4 | 100 ± 4 |
| CorI | 15.6 ± 0.97 | 58.8 ± 2.06 | 10.4 ± 0.62 | 24.6 ± 1.10 | 642 ± 35 | 401 ± 25 | 286 ± 10 | 280 ± 14 |
| CorII | 5.1 ± 0.07 | 38.1 ± 1.21 | 14.6 ± 0.08 | 11.4 ± 0.88 | 576 ± 31 | 322 ± 11 | 205 ± 11 | 127 ± 7 |
| CorIII | 6.1 ± 0.03 | 3.1 ± 0.07 | 22.4 ± 0.13 | 15.3 ± 0.77 | 418 ± 11 | 300 ± 14 | 204 ± 9 | 177 ± 6 |
| GeCI | 46.7 ± 2.61 | 29.6 ± 0.98 | 16.1 ± 0.7 | 12.2 ± 0.75 | 408 ± 29 | 311 ± 21 | 87 ± 4 | 68 ± 2 |
| GeCII | 11.6 ± 0.77 | 6.4 ± 0.07 | 7.4 ± 0.09 | 7.0 ± 0.06 | 340 ± 16 | 293 ± 18 | 74 ± 3 | 61 ± 2 |
| GeCIII | 4.1 ± 0.01 | 4.6 ± 0.05 | 29.6 ± 0.9 | 2.4 ± 0.01 | 334 ± 11 | 127 ± 4 | 103 ± 5 | 83 ± 4 |

[a]Means ± SD of three determinations. For sample codes see Table 1.

drop in the complex phenolic fraction (20). In fact, 3,4-DHPEA is the result of the hydrolysis of the combined phenolic compounds which, given the high antioxidant activity of the *ortho*-diphenol compound, ensures the stability of olive oils over time. During the 18 mon of natural storage [i.e., in green glass in the dark at a mean temperature of 6°C (winter) to 12°C (summer)], no correlations were found between the evolution of the oxidation parameters and the content of natural antioxidants.

After 6 mon of storage, given that the largest amount of 3,4-DHPEA was found at this stage (20), part of the oils was subjected to oven testing to increase the oxidation rate. During oven testing at 75°C, the PV, $K_{232}$, and $K_{270}$ values were monitored until the PV reached 70 meq of active oxygen per kg of olive oil. For each sample, the oven-test period showed a linear increase in PV (Fig. 1) and in $K_{232}$ values (Table 5). The riper the olives, the less resistant the olive oils were to forced oxidation, given their higher slopes in the regression equations of both PV and $K_{232}$ values vs. the number of days of the oven-testing period. Furthermore, these latter values showed appreciable differences between Leccino and Coratina oils, indicating that the former deteriorated more rapidly. The slope of the PV lines, related to the oxidation of the oils, ranged from 0.59 in CorI to 1.32 in LecIII (Fig. 1), whereas the angular coefficients of the $K_{232}$ values ranged from 0.05 in CorI to 0.11 in LecIII (Table 5). The angular coefficients were quite similar in Gentile (Larino) and Gentile (Colletorto) oils, and were included in the Coratina and Leccino values. This behavior was not confirmed by the $K_{270}$ values, which did not vary among the varieties and with respect to the harvest time (Table 5).

Thus, we confirmed that for all varieties, the riper the fruit, the more the thermal oxidative stability of the oils decreased, as measured by means of the PV and $K_{232}$ values (22). Coratina oils were the most resistant to oxidation because of their high total phenol content. This can be attributed to it being a late-ripening variety, a peculiarity of Coratina, as confirmed by the low maturation index values (<1) in the harvest time considered. The Leccino oils at the second and third harvest times were the least stable. This can be explained by their total phenol content (the lowest), related to the high maturation index of the drupes. The stability of the oils after 6 mon of storage, as measured by the number of days needed for PV to reach 70 meq of active oxygen per kg of oil at 75°C, was correlated mainly with the total phenols ($r = 0.89$), and with

**TABLE 5**
**Relationship of $K_{232}$ and of $K_{270}$ with Oven-Testing Period of the Different Virgin Olive Oils[a]**

| | $K_{232}$ | | $K_{270}$ | |
|---|---|---|---|---|
| Samples | Regression equation | $R^2$ | Regression equation | $R^2$ |
| LecI | $K_{232} = 1.5 + 0.06x$ | 0.99 | $K_{270} = 0.22 + 0.008x$ | 0.88 |
| LecII | $K_{232} = 1.6 + 0.10x$ | 0.94 | $K_{270} = 0.15 + 0.012x$ | 0.82 |
| LecIII | $K_{232} = 1.4 + 0.11x$ | 0.93 | $K_{270} = 0.10 + 0.013x$ | 0.89 |
| GeLI | $K_{232} = 1.5 + 0.09x$ | 0.97 | $K_{270} = 0.22 + 0.009x$ | 0.87 |
| GeLII | $K_{232} = 1.7 + 0.06x$ | 0.96 | $K_{270} = 0.15 + 0.007x$ | 0.88 |
| GeLIII | $K_{232} = 1.7 + 0.08x$ | 0.94 | $K_{270} = 0.17 + 0.010x$ | 0.87 |
| CorI | $K_{232} = 1.6 + 0.05x$ | 0.99 | $K_{270} = 0.24 + 0.008x$ | 0.90 |
| CorII | $K_{232} = 1.7 + 0.06x$ | 0.94 | $K_{270} = 0.18 + 0.009x$ | 0.86 |
| CorIII | $K_{232} = 1.7 + 0.07x$ | 0.88 | $K_{270} = 0.25 + 0.010x$ | 0.83 |
| GeCI | $K_{232} = 1.7 + 0.10x$ | 0.96 | $K_{270} = 0.21 + 0.011x$ | 0.90 |
| GeCII | $K_{232} = 1.8 + 0.11x$ | 0.91 | $K_{270} = 0.17 + 0.011x$ | 0.90 |
| GeCIII | $K_{232} = 1.9 + 0.09x$ | 0.93 | $K_{270} = 0.19 + 0.011x$ | 0.89 |

[a]$x$ in days. For sample codes see Table 1.

**TABLE 6**
**α-Tocopherol Content (ppm) in 1 (a) and 6 (b) mon Stored Virgin Olive Oils[a]**

| | α-Tocopherol | |
|---|---|---|
| Samples | a | b |
| LecI | 245.8 ± 11.2 | 187.6 ± 6.4 |
| LecII | 196.9 ± 8.4 | 134 ± 5.4 |
| LecIII | 199.1 ± 7.8 | 145.8 ± 3.9 |
| GeLI | 169.4 ± 5.5 | 141.4 ± 4.8 |
| GeLII | 160.9 ± 6.4 | 118.9 ± 5.1 |
| GeLIII | 178.7 ± 6.8 | 126.7 ± 3.8 |
| CorI | 189 ± 8.6 | 159.4 ± 6.6 |
| CorII | 197.7 ± 5.4 | 161.9 ± 7 |
| CorIII | 194.9 ± 8.3 | 158.1 ± 7.1 |
| GeCI | 182 ± 7.1 | 155.9 ± 4.5 |
| GeCII | 206.7 ± 10.2 | 162.7 ± 5.2 |
| GeCIII | 204 ± 9.4 | 156.1 ± 4.9 |

[a]Means ± SD of three determinations. See Table 1 for sample codes and abbreviation.

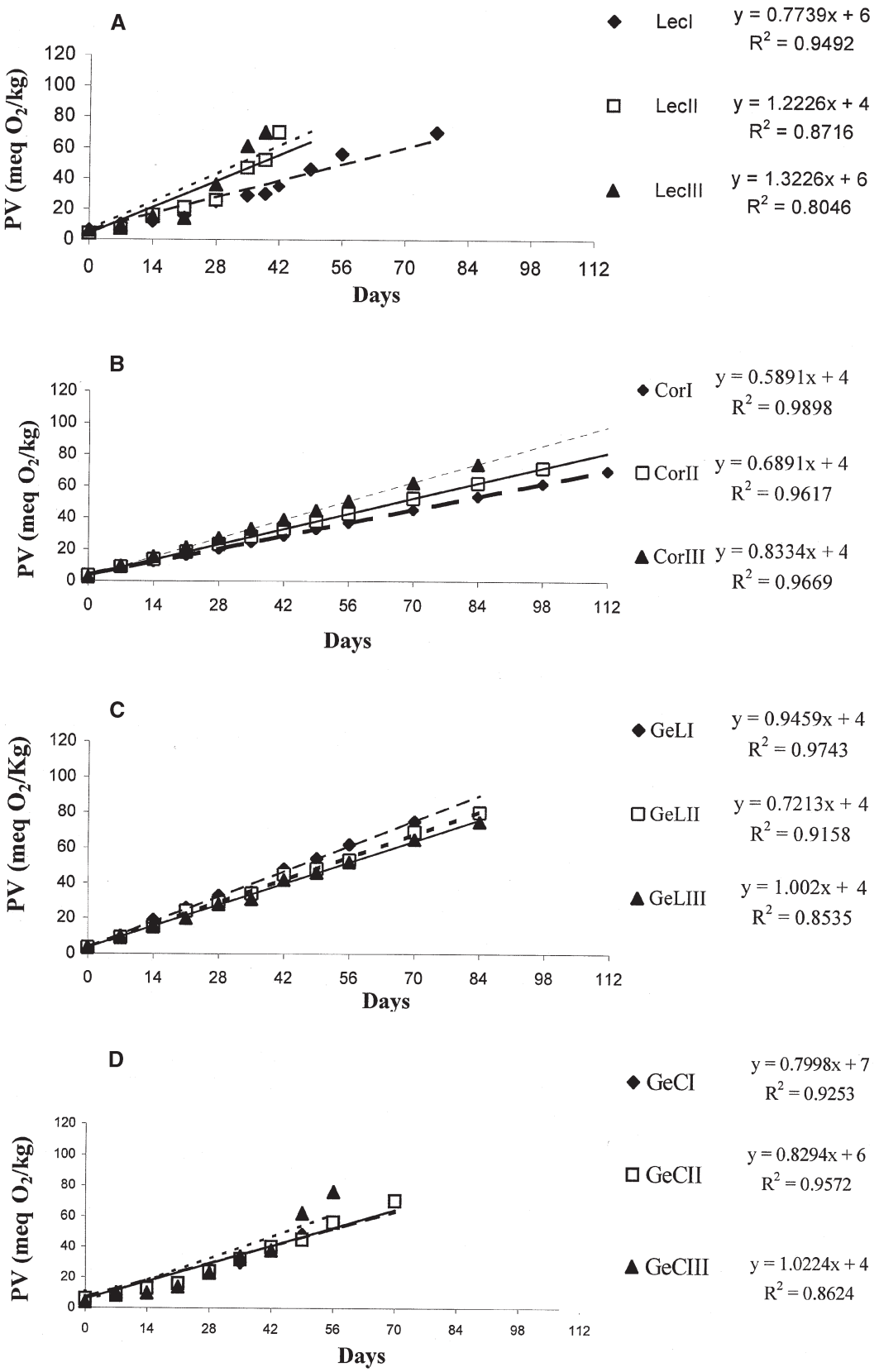


**FIG. 1.** Straight lines, regression equations, and squared correlation coefficients calculated from the relationship between the peroxide values (PV) and number of days of the oven-testing period (days needed to reach 70 meq of active oxygen per kg of oil at 75°C) of the virgin olive oils made from the varieties Leccino (A), Coratina (B), Gentile (Larino) (C), and Gentile (Colletorto) (D), picked at three harvest times: 1 November (I), 15 November (II), and 30 November (III).

the 3,4-DHPEA ($r = 0.80$) contents. Last, α-tocopherol content (Table 6) changed significantly after 6 mon of natural storage (*t*-paired value: 12.37; $\alpha = 0.0001$), but there were no significant variations as regards the varieties and harvest times, and between oil stability and α-tocopherol. Probably, as reported elsewhere (9), the action of α-tocopherol in the presence of large amounts of phenols did not have a notable additional antioxidant effect.

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