Influence of Fruit Ripening on Olive Oil Quality

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Olives (*Olea europaea* cv. Arbequina, Blanqueta, Lechín, Villalonga, and Verdial) used for oil production were harvested and distributed in four successive stages of ripening according to their skin color (green, spotted, purple, and black). The firmness of the fruits and the quality of the oils extracted from these fruits were analyzed. The resistance to postharvest handling measured by fruit firmness decreased during fruit ripening. The total oil content, the total oil extracted, and the α-tocopherol content did not change appreciably during this process. In general, the parameters which measure the oxidation of the oils extracted (K_{230}, K_{270}, and stability to oxidation) indicated a progressive deterioration of oil quality as fruit ripening progressed. Moreover, in this process bitterness indices decreased in the oils. The stage of ripening mainly affected the sensory quality of the oils obtained from the Verdial and Blanqueta varieties, which clearly decreased during fruit ripening.

Keywords: *Olea europaea; maturity; postharvest; oil quality; analytical determinations*

INTRODUCTION

The quality of olive oil is strongly related to the physiological conditions of the fruit from which it was extracted. The action of parasites, such as the olive fly, prior to harvest or fungal activity during the period between harvest and oil extraction are, in general, the main external agents responsible for the breakdown of metabolic processes in the olive and subsequent reduction in oil quality (Kiritsakis, 1991; Castellano et al., 1993). Furthermore, there is an important internal cause of deterioration: the age of the fruit. The stage of ripening may directly or indirectly affect oil quality. The fruit physiology undergoes changes directly related to the age, and these changes alter the oil quality. Furthermore, there is an indirect effect provided by the action of external agents of deterioration which increase during fruit ripening (Humanes, 1976). As a result of these effects, only 6% of the olive oil produced is of the best commercial quality (Luchetti, 1993).

Olive ripening begins after a period of 25 weeks of cell growth. In this time, the fruit has developed its final size, maintaining the original green skin color. This first stage of ripening is thus known as the "green stage" corresponding to green mature fruits. Subsequently, chlorophyll pigments in the olive skin are progressively replaced by anthocyanines during fruit ripening (Barranco et al., 1988). This fact allows the process of ripening to be divided into stages according to the concentration of anthocyanines exhibited. Thus, it is possible to identify a "spotted stage", a "purple stage", and a "black stage" according to the skin color of the fruits (Uceda and Frías, 1975).

Lipid biosynthesis mainly occurs during cell growth of the olive fruit. This activity concludes with the beginning of ripening (García and Mancha, 1992). Harvesting of fruit at the green stage of ripening does not imply a loss of oil yield and would allow an easier postharvest handling of the fruit because green olives are more resistant to mechanical damage and fungal infection than olives in subsequent stages of ripening. However, the oils obtained from green olives are excessively bitter. This does not imply automatic rejection of the oil since olive oils are normally bitter, but if the level of bitterness is too high it could cause problems for consumer acceptance (Gutiérrez et al., 1992).

To date, the optimal date for harvesting olives for oil production has been selected using traditional rather than scientific criteria. The studies on harvesting are complicated by the different behaviors shown by the distinct olive varieties (Boschelle et al., 1994). Maxie (1964) and Woskow and Maxie (1965) found different table olive varieties to give different physiological responses to storage conditions. The mill olive varieties also follow different trends in their physiology and in the quality of the oil obtained from them. Thus, the oils obtained from var. Picual olives are more stable to oxidation than the oils obtained from var. Arbequina fruits (Humanes and Civantos, 1992).

In this work, the influence of the stage of fruit ripening on the parameters which measure oil quality is described, using five mill olive varieties, for evaluating the contribution of each stage of ripening to the overall oil quality. At the same time, this criterion may be useful for the selection of an optimum harvesting date for each variety.

MATERIALS AND METHODS

Olive fruits (*Olea europaea*), cv. Arbequina, Blanqueta, Lechín, Villalonga, and Verdial, were harvested in different orchards, and each cultivar was transported the same day to the experimental mill of the Instituto de la Grasa for olive oil extraction. There, about 60 kg of olives was randomly taken from each variety. The olives were distributed in four ripening groups according to their skin color (green, spotted, purple, or black), for each variety. Only healthy fruits, without any kind of infection or physical damage, were selected. Resistance of the flesh to deformation was determined in 100 olives from each ripening group and variety using a Zwick 3300 densimeter (Zwick Gmbh & Co., Ulm, Germany) with a 5 mm diameter disk (force required to depress the disk 2.4 mm into the fruits), and the result is expressed in N/cm^2.

The total oil content was determined in triplicate in samples of 30 g of olives previously dried under vacuum to constant weight and ground. The samples were extracted with hexane in a Soxhlet extractor for 5 h, and the results are expressed as percentage of dry weight. The oil from 4 kg of olives from each group was extracted separately in triplicate using an Abencor analyzer (Comercial Abengoa S.A., Sevilla, Spain). This unit consists of three basic elements: a mill, a thermo-

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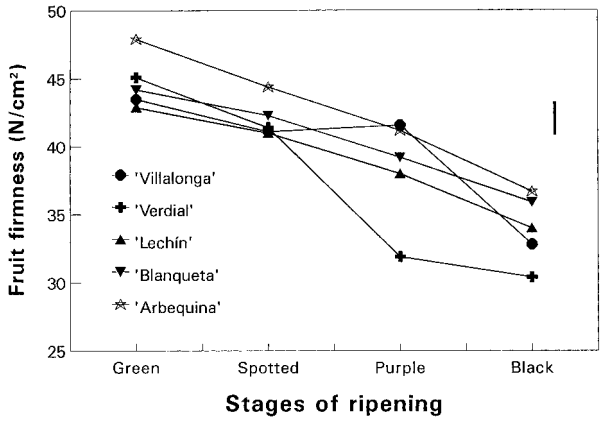

Figure 1. Fruit firmness (N/cm^2) of olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

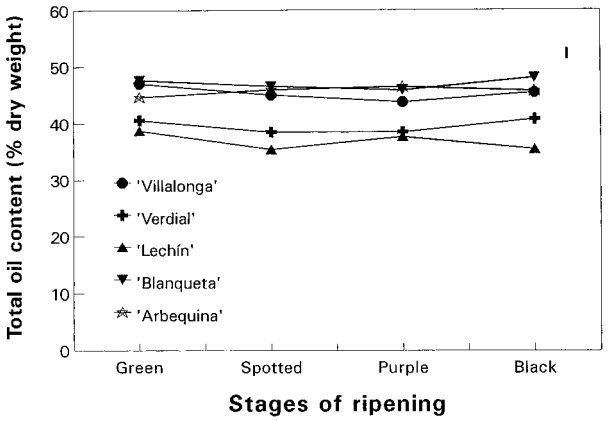

Figure 2. Total oil content (measured as % dry wt) of olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

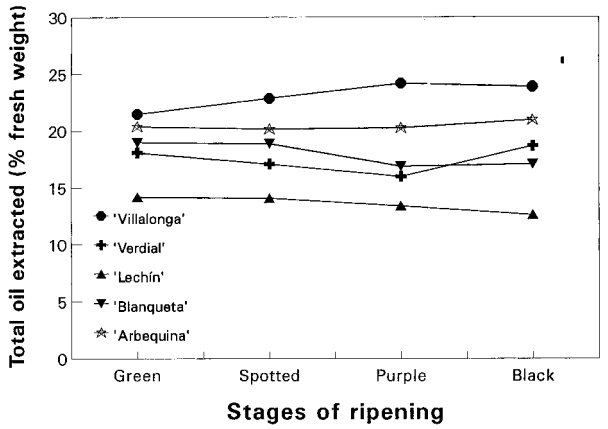

Figure 3. Total oil extracted (measured as % fresh wt) from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

beater, and a pulp centrifuge (Martínez et al., 1975). The oil was separated by decanting and the amount obtained evaluated. The results are expressed as percentage of fresh weight.

The titratable acidity and the coefficients of specific extinction at 232 and 270 nm (K_{232} and K_{270}) were determined from the extracted oils according to the UNE standard Spanish methods (AENOR, 1973a,b). Acidity value, given in percent of oleic acid, was determined by titration with 0.1 N KOH of a solution of oil (20 g) in a previously neutralized solvent (ethanol:ethyl ether, 1:1) and a phenolphthalein indicator (1% in ethanol). K_{232} and K_{270} extinction coefficients (absorption of a 1% solution of oil in cyclohexane at 232 and 270 nm, respectively, with a 1 cm path length) were measured on a UV spectrophotometer (Hitachi U-1100).

Resistence of the oils to oxidation was measured by the Rancimat method (Läubli and Bruttel, 1986; Gutiérrez, 1989). Evaluation of bitterness was carried out using the coefficient of specific extinction of the oils at 225 nm, according to the method of Gutiérrez et al. (1992). This methodology allows to isolate minor polar compounds, including polyphenols, which are responsible for the bitter taste of the olive oil. The content in these compounds can be measured to 225 nm and is closely related with the intensity on bitter taste measured by an analytical panel of tasters. The α-tocopherol content of the oil samples was measured by HPLC using the method of IUPAC (1992).

Sensorial quality of each oil sample was evaluated by a 12-member analytical panel of the Instituto de la Grasa, according to the method described in Annex XII of the European Economic Community Rules (2568/91). Each oil was graded according to a scale of 9 points, 1 being the value for very poor quality and 9 for optimum quality.

Analysis of variance was carried out on all data. A 5% level of least-significant difference (lsd), calculated by Duncan's multiple range test, was employed to establish differences between the means obtained for the treatments.

RESULTS AND DISCUSSION

As is usual in fruits, firmness decreased with olive ripening (Figure 1). However, each variety showed a different softening profile. While cv. Arbequina, Blanqueta and Lechín in that order, from higher to lower firmness values, showed a parallel loss of firmness, cv. Verdial and Villalonga softened sharply at the purple and black stages, respectively. The firmness gives an approximate idea about the suitability of a fruit for storage. Soft olives are very susceptible to mechanical damage and pathogenic infection and must be processed as soon as possible because they very rapidly lose the initial quality of the oil obtained from them (García and Streif, 1991). If a delay in oil extraction is foreseeable, the olives must be harvested before the percentage of purple and black fruits becomes significant in the crop. This fact is especially important for the Verdial variety, which shows premature softening.

The oil contents remained practically unchanged in the ripening stages of the varieties assayed (Figure 2). This observation agrees with the results published by García and Mancha (1992). The latter authors found no lipid biosynthesis in olives of the Picual and Gordal varieties harvested 25 weeks after flowering, when fruits had a green mature appearance. Therefore, processing a crop with more black fruits does not imply that more oil will be obtained. The varieties studied can be perfectly classified into two groups according to their oil content: a first group formed by the Arbequina, Blanqueta, and Villalonga varieties (mean oil content 47%) and a second group with significantly lower ($P \leq 0.05$) values formed by the Verdial and Lechín varieties (mean oil content 39%).

As a consequence of the stable oil content, the oil extracted also only varied very slightly during the different ripening stages of the olives (Figure 3). Nevertheless, the differences between varieties were more evident when the amount of oil extracted was considered than when oil contents were considered. The varieties appear ranked according to this parameter. Cv. Villalonga showed significantly higher ($P \leq 0.05$) values than the other olives; cv. Arbequina occupied a second place with significantly higher ($P \leq 0.05$) values than the group formed by cv. Blanqueta and Verdial; finally, cv. Lechín showed significantly lower ($P \leq 0.05$) values.

With the exceptions of the oils obtained from cv. Villalonga olives, which showed a slight decrease, and

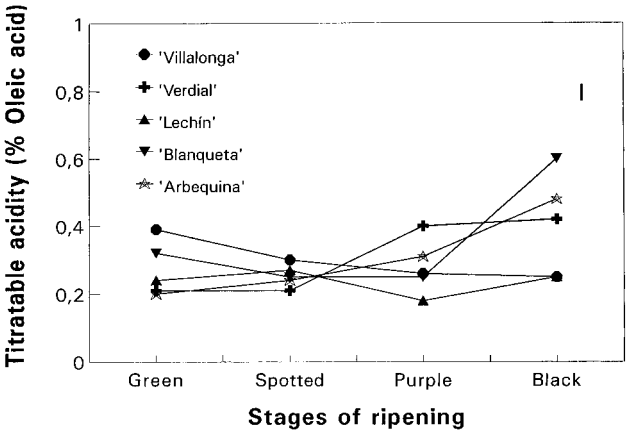

Figure 4. Titratable acidity (% oleic acid) of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

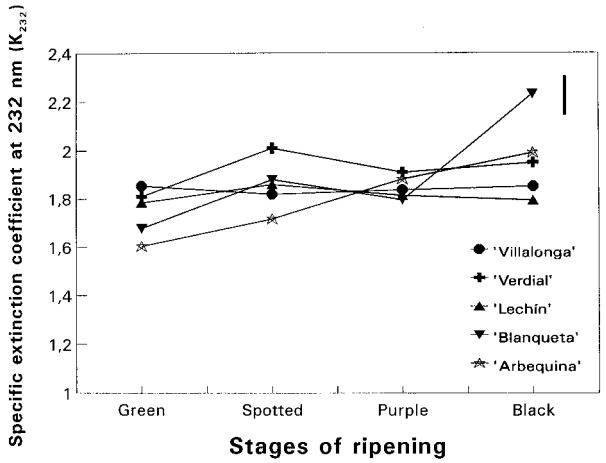

Figure 5. Specific extinction coefficients at 232 nm (K_{232}) of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

of the oils extracted from cv. Lechín, which maintained their initial values, the majority of the oils exhibited an increase in their titratable acidity as ripening progressed (Figure 4). Particularly important was the increase shown in the amount of oil obtained from black olives of the Blanqueta variety as compared to that obtained from purple fruits of the same variety. The values obtained were lower than the limit (1%) accepted for the titratable acidity of the best commercial quality olive oil (designated "extra"). This fact is due to the use of only healthy fruits in the experiment and to their rapid processing. From an industrial point of view, where the selection of healthy olives is not possible and delays in processing are frequent, olives at later stages of ripening should give oils with higher levels in titratable acidity, since they are more sensitive to pathogenic infection.

In general, the oils obtained from olives at more advanced ripening stages showed an increase in the content of conjugated fatty acids, measured by their K_{232} (Figure 5). Only the oils from cv. Villalonga maintained similar values in all the ripening stages analyzed. Black cv. Blanqueta olives gave an oil with a significantly higher ($P < 0.05$) value for this parameter (2.20) than the rest of the samples (mean 1.80). As the limiting value for "extra" olive oil (2.40) is approached, harvesting of cv. Blanqueta olives should be carried out before the percentage of black fruits reaches a high level.

Changes in the carbonyl (aldehydes and ketones) contents of the oils obtained from olives at more

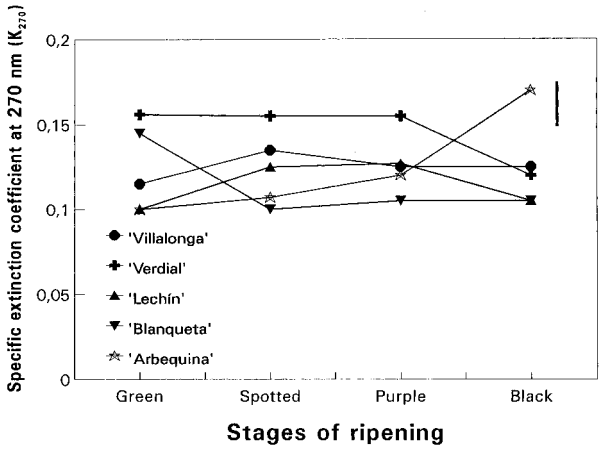

Figure 6. Specific extinction coefficients at 270 nm (K_{270}) of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

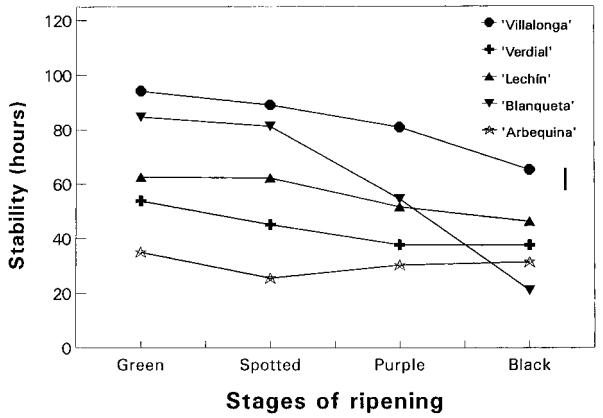

Figure 7. Stability to oxidation (h) of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

advanced stages of ripening, measured by their K_{270}, differed according to the variety, following distinct profiles (Figure 6). The oils obtained from cv. Arbequina olives had increasing values as ripening progressed, showing the lowest K_{270} at the green stage (0.10) and the highest value (0.17) at the black stage, this value being significantly higher ($P \leq 0.05$) than the ones shown by the oils extracted from the other varieties at the same ripening stage. In contrast, the cv. Blanqueta olives at the green stage gave oils with a greater carbonyl content, and subsequently, the oil obtained from spotted fruit lost 30% of the former value. The oils extracted from the cv. Lechín and Villalonga olives showed similar values throughout ripening. Finally, cv. Villalonga fruits at the three stages mentioned above gave oils with a relatively high K_{270} (0.16), while the black olives gave an oil with a significantly lower ($P \leq 0.05$) value. These trends probably arise as a result of different metabolic responses in the last stages of the fatty acid oxidation pathway in the varieties studied. The limiting value of K_{270} established for "extra" quality oil (0.20) was not, however, exceeded by any sample.

The study of the stability to oxidation of the oils extracted from olives at different stages of ripening allows the different varieties used to be ranked (Figure 7). In general, the values decreased slightly as fruits ripened. The oils obtained from cv. Blanqueta olives represented an exception to this general rule, showing a sharp loss of stability after the purple stage. The highest stability was shown by the oils extracted from the cv. Villalonga olives followed by the oils from cv.

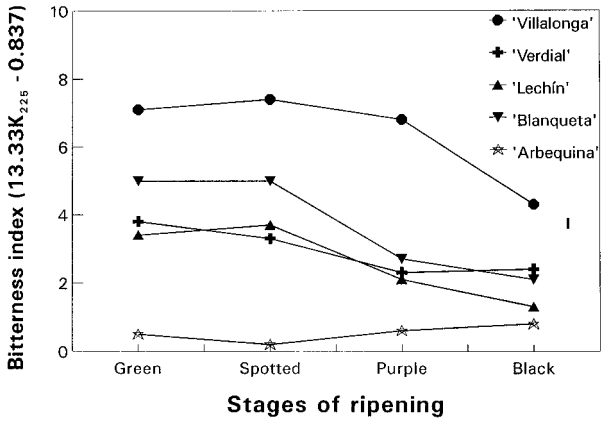

Figure 8. Bitterness indices, measured by their extinction coefficients at 225 nm (K_{225}), of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

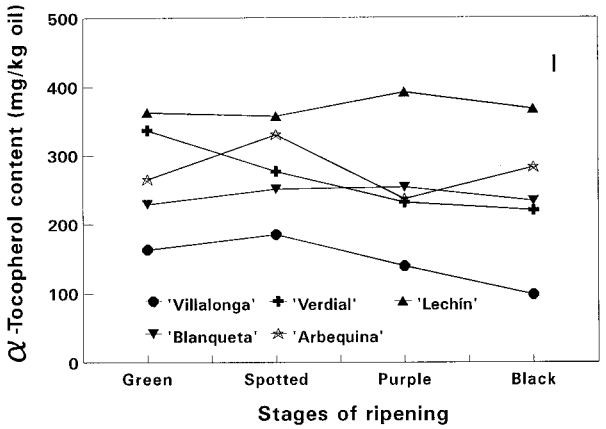

Figure 9. α-Tocopherol contents of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

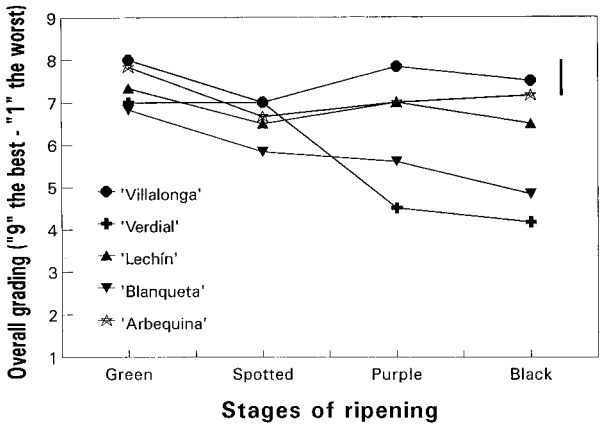

Figure 10. Sensory evaluation (overall grading on a subjective scale, where 9 is the best quality and 1 the worst quality) of oils obtained from olives at different stages of ripening. Vertical bar represents least-significant difference at $P \leq 0.05$.

Blanqueta, although the oil extracted from black fruits of this variety showed the poorest stability. The oils from cv. Lechín and Verdial occupied, in that order, an intermediate position, and the lowest mean value was shown by the oils from the cv. Arbequina olives. The olive variety and the ripening level are factors that need to be seriously considered when aiming for a suitable oil stability.

In general, the bitterness index of the oils decreased as the ripening progressed (Figure 8). Only cv. Arbequina olives broke this rule, giving oils with low levels of bitterness from the start of the ripening. The high values reached by oils extracted from cv. Villalonga olives set them in a separate group. The rest of the varieties assayed gave intermediate values. The similarity between the changes in the bitterness index and the stability to oxidation of the oils obtained (Figures 8 and 7) is also noteworthy. This fact arises because both parameters are related to the polyphenol content. These compounds act as natural antioxidants in olive oil (Chimi et al., 1988) and are responsible for the oil bitterness. They are, therefore, the factors mainly responsible for oil absorbance at 225 nm (Gutiérrez et al., 1992). The oils obtained from cv. Villalonga olives showed a high level of bitterness. There was only a significant ($P \leq 0.05$) decrease in this parameter, if the oil was extracted from black olives, but even then the level of bitterness was high. Therefore, from a commercial point of view, blending cv. Villalonga oil with other oils of a low level of bitterness, such as that obtained from cv. Arbequina, would avoid the problem of excessive bitterness and would contribute to increasing the stability of the second oil, since both parameters appear additive. The oils from Blanqueta, Lechín, and Verdial varieties showed a significant ($P \leq 0.05$) decrease in bitterness when they were extracted from purple olives. Subsequently, this decrease continued but less sharply. The oils obtained from the cv. Arbequina olives showed a very low level of bitterness. Therefore, for this variety, a later harvesting does not represent any advantage.

The α-tocopherol content of the oils extracted from olives at different stages of ripening varied only slightly between the different varieties studied (Figure 9). However, the Verdial and Villalonga varieties exhibited a significant ($P \leq 0.05$) decrease in α-tocopherol content as ripening progressed. This parameter also ranked the varieties in three clearly differentiated groups. The highest values were shown by the oils obtained from cv. Lechín olives during the process of ripening, and these formed a first group. In intermediate place are the Arbequina, Blanqueta, and Verdial varieties, which form a second group. Finally the third group is constituted by the Villalonga variety, which showed significantly lower ($P \leq 0.05$) values. The different profiles shown by the olives in α-tocopherol content and stability to oxidation (Figures 9 and 7) demonstrate that the action of α-tocopherol as a natural antioxidant in olive oil is secondary in comparison to the effect of the polyphenol content.

The results obtained for the sensory analysis of the oils (Figure 10) allow the varieties studied to be divided in two groups according to the different behavior they exhibit during the ripening of the fruits from which they were extracted. The evaluation of the oil quality from Blanqueta and Verdial varieties decreased significantly ($P \leq 0.05$) as ripening progressed. The limit established for "extra" quality olive oil (6.5) was lost by the oils obtained from spotted cv. Blanqueta olives and purple cv. Verdial olives. For these two varieties, the selection of a suitable harvest date is very important if the best oil quality is to be obtained from the sensory analysis point of view.

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LITERATURE CITED

Aenor. Asociación Española de Normalización y Certificación. Spanish standard UNE 55011-73; Madrid, 1973a.

Aenor. Asociación Española de Normalización y Certificación. Spanish standard UNE 55047-73; Madrid, 1973b.

Barranco, D.; Milona, G.; Rallo, L. Epocas de floración y maduración de variedades de olivo. (Flowering and maturation seasons of olive varieties). Proceeding of III Congreso Nacional de la Sociedad Española de Ciencias Hortícolas, Tenerife, Spain, 1988.

Boschelle, O.; Mozzon, M.; Giono, A. Aceite virgen extra típico Cuáles son sus perspectivas en Fiuli-Venezia Giulia? (Typical virgin olive oil. Which are its perspectives in Fiuli-Venezia Giulia?). *Olivae* **1994**, *50*, 31−35.

Castellano, J. M.; García, J. M.; Morilla, A.; Perdiguero, S.; Gutierrez, F. Quality of `Picual` olive fruits stored under controlled atmosphere. *J. Agric. Food Chem*. **1993**, *41*, 537−539.

Chimi, H.; Sadik, A.; Le Tutour, A.; Rahmani, M. Contribution à l'étude comparative des pouvoirs antioxydants dans l'huile d'olive du tyrosol de l'hydroxytyrosol, de l'acide cafeique, de l'oleuropeine et du BHT. (Contribution to the comparative study about the antioxidant power of tyrosol, hydroxytyrosol, cafeic acid, oleuropeine and BHT in olive oil.) *Rev. Fr. Corps Gras* **1988**, *35*, 339−344.

García, J. M.; Streif, J. The effect of controlled atmosphere storage on fruit and oil quality of 'Gordal' olives. *Gartenbauwissenschaft* **1991**, *56*, 233−238.

García, J. M.; Mancha, M. Evolución de la biosíntesis de lípidos durante la maduración de las variedades de aceituna 'Picual' y 'Gordal'. (Evolution of the lipid biosynthesis during the maturation of the olive varieties Picual and Gordal). *Grasas Aceites* **1992**, *43*, 277−280.

Gutiérrez, F. Determinación de la estabilidad oxidativa de aceites de oliva vírgenes: Comparación del Método del Oxígeno Activo y el método Rancimat. (Determination of the oxidative stability of virgin olive oils: comparison of the active oxygen and the Rancimat methods). *Grasas Aceites* **1989**, *40*, 1−5.

Gutiérrez, F,; Perdiguero, S.; Gutiérrez, R.; Olías, J. M. Evaluation of the Bitter taste in virgin olive oil. *JAOCS* **1992**, *69*, 394−395.

Humanes, J. Aceite de oliva de calidad. Influencia del cultivo. (Olive oil quality. Influence of culture conditions). *Agricultura* **1976**, *660*, 506−509.

Humanes, J.; Civantos, M. *Producción de aceite de oliva de calidad. Influencia del cultivo.* (Production of high quality olive oil. Influence of culture conditions). Junta de Andalucía: Sevilla, Spain, 1992.

IUPAC. *Standard method for the analysis of oils, fats and derivatives. Method 2,432*, 7th ed; Pergamon Press: Oxford, 1992.

Kiritsakis, A. K., Ed. *Olive oil*; American Oil Chemists' Society: Champaign, IL, 1991.

Läubli, W.; Bruttel, P. A. Determination of the oxidative stability of fats and oils by the Rancimat method. *JAOCS* **1986**, *63*, 792−794.

Luchetti, F. El COI y la mejora de la calidad. (The International Olive-oil Council (IOC) and the improvement of olive-oil quality). *Agricultura* **1993**, *730*, 384−385.

Martínez, J. M.; Muñoz, E.; Alba, J.; Lanzón, A. Informe sobre utilización del analizador de muestras Abencor. (Report about the use of the "Abencor" analyzer. Abencor). *Grasas Aceites* **1975**, *26*, 379−385.

Maxie, E. C. Experiments on cold storage and controlled atmosphere. 43rd Annual Technical Report of the California Olive Association, Davis, CA, 1964; pp 12−14.

Uceda, M.; Frías, L. Epocas de recolección. Evolución del contenido graso del fruto y de la composición y calidad del aceite. (Seasons of harvest. Changes on fruit oil content, oil composition and oil quality). *Proceeding of II Seminario Oleícola Internacional*; International Olive-oil Council: Cordoba, Spain, 1975.

Woskow, M.; Maxie, E. C. Cold storage studies with olives. 44th Annual Technical Report of the California Olive Association, Davis, CA, 1965; pp 6−8.

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