Quality characteristics of Cornicabra virgin olive oil

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ABSTRACT. This review examines the composition of Cornicabra virgin olive oil, some of the factors that may affect it, like fruit ripening and extraction system, and their relation with quality. The main characteristics of Cornicabra oil were: high oleic acid (80.4 ± 1.0%, as mean and standard deviation) and low linoleic acid content (4.5 ± 0.6%); high campesterol level (4.2 ± 0.2%), exceeding the EU Regulation upper limit of 4%; large total phenols content (ranging from 20 to 380 mg/kg as caffeic acid), and great Rancimat oxidative stability (from 10 to 140 h). Sensory evaluation showed that the total score of 35% of Cornicabra olive oils was lower than the limit of 6.5 established for the ‘extra-virgin’ category. The majority of the analytical parameters, i.e. peroxide value, K₂₇₆, pigments, sensory scores, oleic acid and total sterols, diminished during ripening, whereas free acidity, linoleic acid and Δ-5-avenasterol increased. The behavior of oil extraction yield, oxidative stability, natural antioxidants and campesterol was more complex. The evolution of the analytical parameters studied suggests that the best stage of maturity of Cornicabra olive fruits for processing is a ripeness index higher than 3.0 and lower than 4.0-4.5. With respect to extraction system and crop season, only minor differences, although some of them statistically significant, were observed in the quality indexes of the Cornicabra virgin olive oil.

Olive cultivation originated in Asia Minor and spread to Greece, Italy, Spain and Northern Africa. Virgin olive oil’s characteristic aroma, taste and color distinguish it from other edible vegetable oils. It is one of the edible fats most highly prized by Mediterranean peoples and therefore constitutes a fundamental component of their diet. It can be consumed without any kind of refining process and thus retains its natural flavor and aroma, and it also possesses highly-appreciated nutritional characteristics thanks to its balanced composition of fatty acids and natural antioxidants (1, 2). Olive oil is widely used as a condiment, cooking medium or emulsion component and in the storage of vegetable and animal foods; also, the current tendency for consumers to select the least-processed foods has prompted a re-assessment of its consumption in the regular diet in many countries.

The chemical and quality characteristics of a virgin olive oil are determined by a series of factors like the nature of the soil, the climate, variety of the plant, cultivation, oil extraction techniques and storage conditions. It is a matter of great concern for the olive oil industry to preserve its excellent organoleptic and nutritive properties.

A major effort has been made in recent years by the main olive oil producing countries to study the chemical composition of major and minor components and their relation with oil quality, and to try and establish analytical determinations that can effectively identify olive oil varieties or oil produced in a specific area (3-9). In Spain, some of the most important olive varieties such as Picual, Hojiblanca and Arbequina from the regions of Andalucía and Cataluña have been exhaustively studied (10-14). However, despite the economic importance of the Spanish Cornicabra variety of olive oil, until recent years the scientific literature contained no complete and reliable data on its chemical composition and properties from a large enough number of successive crop seasons to be statistically
relevant.

The Cornicabra olive variety is the most common in the region of Castilla-La Mancha. It covers an area of 300,000 Ha, mainly in the provinces of Ciudad Real and Toledo, and accounts for more than 14% of the olive oil produced in Spain. The fruit is medium to large with a characteristically elongated and asymmetric shape. The fat yield is 22-24% of fresh weight and the oil is valued for its high stability and good sensory characteristics, such as a dense sensation and a balanced aroma, sour and pungent (15-18).

This review discusses the analysis of the chemical composition of Cornicabra virgin olive oil from five successive crop seasons (from 94/95 to 98/99), together with some of the factors that may affect the concentration of major and minor components in the oil, like the stage of maturity of the olive fruit and the extraction system employed, and their relation with quality characteristics. Several series of analytical determinations were chosen: quality indexes as defined by EU Regulations (free fatty acid content, peroxide value, spectrophotometric characteristics in the UV region and sensory evaluation), which can also be used for law enforcement; parameters of interest involved in oxidation processes (oxidative stability, phenols, tocopherols and chlorophyll and carotenoids pigments); fatty acid and sterol composition.

CHEMICAL COMPOSITION AND QUALITY INDEXES.

Quality and genuineness criteria for various olive oil types are described in detail in the EU Regulations, EEC/2568/91 and later modification EEC/656/95 (19).

For the majority of the Cornicabra virgin olive oils analyzed, the values of the analytical parameters fell within the ranges established for the highest quality category ‘extra virgin’ olive oil (16, 18).

Free acidity. Acidity is the first objectively-determined criterion applied to olive oil and was introduced at the beginning of the century. The quantity of free fatty acids is an important quality factor and has been extensively used as a traditional criterion for classifying olive oil in various commercial grades. Free fatty acid content in the Cornicabra oil ranged from 0.1 up to 1.8%, expressed as percentage of oleic acid, with a median value of 0.5 (18). Only 10% of the oils analyzed showed more than 1% free acidity, the upper threshold limit for the ‘extra-virgin’ category (EU Regulations), and none exceeded the limit of 2% for the ‘virgin’ category. It is known that the increase of free acidity is mainly due to enzyme activity favored by olive tissue damage (1).

Peroxide value and UV characteristics. The peroxide value evaluates hydroperoxides content and offers a measure of lipid oxidation. In the samples studied, the peroxide value presented a median value of 8 meq O₂ per kg, and a range between 4 and 30 (18). Less than 5% of the oils had a peroxide value higher than the upper limit of 20 established for the ‘extra-virgin’ olive oil.

UV spectrophotometric characteristics are measurements of extinction coefficients (E₁%₁ cm) at 232 and 270 nm, that correspond to the maximum absorption of the conjugated dienes and trienes. High UV extinction coefficients are due either to the presence of oxidation or cleavage products formed during storage, or to the effect of refining. Less than 2% of the oils studied had K₂32 or K₂70 values higher than the limits established for ‘extra-virgin’ olive oil (18).

Oxidative stability and antioxidants. Deterioration of oil quality is mainly due to oxidation caused by the high reactivity of free radicals to fatty acids (20). Although rapid methods of assessing the oxidative stability of oils, like the Rancimat apparatus (21), which correlates well with the active oxygen method (22), have been introduced, none of the established determinations have been reported to correlate well with the shelf life of olive oil. The resistance of virgin olive oil to autoxidation is related to the high levels of monounsaturated triacylglycerols and the presence of natural antioxidants. However, the exact role of individual compounds has not yet been firmly established. Oxidative stability of the Cornicabra olive oils analyzed ranged from a minimum of 10 h to a maximum of 140 h, with a median value of 60 h (18). A quarter of the samples exhibited stability in excess of 80 h, while in another quarter stability was less than 40 h. According to these results and published data on other Spanish varieties (14), Cornicabra and Picual
are the two Spanish olive varieties whose oils are most stable to oxidation. A properly prepared Cornicabra olive oil extracted by centrifugation using good quality olives can easily attain stability upward of 100 hours, as observed in the oil prepared in the pilot plant at this University.

Virgin olive oil contains phenolic substances which affect its stability and contribute to oil flavor and aroma (23-25), especially to the typical bitter taste of olive oil (26). Phenolic compounds present in olive oil are conventionally denominated “polyphenols” and are part of the polar fraction which is usually obtained from the oil by extraction with methanol-water. This fraction is a complex mixture and its chemical nature has not been completely elucidated (27-31). The median content of total phenol compounds in the samples analyzed was 150 mg/kg (as caffeic acid), although a wide range of concentrations was observed, from 20 up to 380 (18). Twenty per cent of the oils contained more than 200 ppm of phenols, and 10% contained less than 100 ppm. As was found with respect to oxidative stability, the polyphenol content of the Cornicabra variety (together with Picual) is among the highest of all Spanish olive oils (32, 33).

It is known that the behavior observed in stability is influenced by some phenolic compounds (17, 34-37). A high correlation (from 0.87 to 0.96), consistent through the five seasons, has been observed in Cornicabra olive oil between total phenol content and oxidative stability by Rancimat (18). A good direct correlation between oxidative stability and total phenols content determined by a colorimetric method has also been reported by many authors (29, 34, 38), but it is not yet sufficiently clear what individual phenolic compounds are mainly responsible for the antioxidant activity. The correlation between α-diphenols and Rancimat stability was slightly lower than with total phenols for commercial virgin olive oils in all cases (18), as observed also by Aparicio et al. (33).

The α-tocopherol content in the Cornicabra variety oils studied ranged from 50 up to 320 mg/kg, with a median value of 170 mg/kg (18). Cornicabra olive oil apparently has slightly lower tocopherol content than other Spanish varieties (12). The tocopherol content is highly variety-dependent, with concentrations ranging from 5 to 300 ppm. Usual values reported for good quality oils vary between 100 and 300 ppm (39, 40). There are discrepancies concerning the role of α-tocopherol in the olive oil autoxidation (41).

**Pigments: chlorophylls and carotenoids.** The natural pigment contents of the oils are important quality parameters because they correlate with color, which is a basic attribute for evaluating olive oil quality, although this is not required by EU Regulations. Virgin olive oil has a color from green-yellow to gold, depending on the variety and the stage of maturity. Pigments are also involved in autoxidation and photo-oxidation mechanisms (42, 43). Chlorophyll and carotenoids in Cornicabra oils have been found to range from 2 to 30 ppm and from 2 to 15 ppm respectively (18), as expected for virgin olive oils from Spanish varieties (44).

**Sensory analysis.** Organoleptic properties are the oldest criterion employed for distinguishing the quality of an oil. According to the method described in the EU Regulation (19), the oils are evaluated on a 0-9 point scale, which is related to the perception of the characteristic flavor stimuli, especially ‘fruitiness’, and the absence of defects, as judged by a group of selected and trained tasters working as an analytical panel. Results of a sensory evaluation indicated that the total score in 35% of Cornicabra virgin olive oils studied was lower than the limit of 6.5 established for the ‘extra-virgin’ category (18). Total scores ranged from 6.0 to 7.3, with a median value of 6.7. This means that although the majority of the chemical parameters fell within the limits established for the maximum olive oil category, and only 10% of the commercial oils were classified as ‘virgin’ for exceeding free acidity limits, significantly more of these olive oils failed the minimum sensory requirements for the highest category. Fruitiness scores ranged from 1.5 to 2.6, whereas the scores for pungency and bitterness, two positive attributes peculiar to Cornicabra virgin olive oil, ranged from 0.9 to about 3.7. The pattern was similar for intensity of bitterness as defined by Gutierrez et al. (26), as opposed to sensory bitterness. The oils obtained from green olives were excessively bitter according to the panelists’ comments. This does not imply
rejection of the oil, but if the level of bitterness is too high it could cause problems for consumer acceptance.

Fatty acid composition. The distribution of fatty acid composition of the oil samples studied covered the normal range expected for olive oil. Cornicabra oil has a high percentage of oleic acid, with a median value of 80.6 and an interquartile range of 1.3 (difference between 75th and 25th percentiles), and a low percentage of linoleic acid, with a median value of 4.5 and an interquartile range of 0.7 (18). Cornicabra and Picual are the Spanish varieties with the lowest linoleic acid levels (45). Primary known factors affecting fatty acid composition, especially the oleic acid content, are latitude, climate, variety and stage of maturity of the olives when collected (5).

Sterol composition. Sterols are important nonglyceridic constituents of olive oil because they relate to the quality of the oil and are widely used to check genuineness. In the Cornicabra variety the main sterols are β-sitosterol, Δ5-avenasterol and campesterol. All the oil samples analyzed showed high campesterol content, with a median value of 4.2% and an interquartile range from 4.1 to 4.3, which exceeded the threshold established by EU Regulations (4%) (18). Campesterol content was below this threshold in less than 10% of the oils studied, so that it is clearly a peculiarity of this olive oil variety. Another unusual feature of the Cornicabra and Hojiblanca varieties is high Δ5-avenasterol content (45, 46), with a mean value of 6.2%, which has been associated with antioxidant activity (47). All of the Cornicabra oils contained more than 1000 mg/kg of total sterols, the minimum value established by EU Regulations for the ‘extra virgin’ olive oil category, with a median value of 1520 mg/kg. In the case of apparent β-sitosterol, about the 15% of the samples contained less than the threshold value of 93%.

Overall quality index. To express virgin olive oil quality numerically, an Overall Quality Index (OQI) was adopted by the International Olive Oil Council in 1990 (48). This is a scale from zero to ten that considers four quality parameters: the score for sensory evaluation (SE), free acidity (FA), K270, and peroxide value (PV), according to the following equation:

\[ OQI = 2.55 + 0.91SE - 0.78FA - 7.35K_{270} - 0.066PV. \]

Factors negatively affecting virgin olive oil quality are mainly connected with damage to olive fruit tissues; this stimulates enzymatic and microbiological activities, in particular lipolytic and oxidative processes, which increase the free acidity, K270 and peroxide values.

INFLUENCE OF FRUIT RIPENING.
The olive fruits take several months to ripen, and development varies according to the growing area, olive variety, temperature and cultural practices. During ripening, important chemical changes occur inside the drupe which are related to the synthesis of organic substances, especially triglycerides, and to other enzymatic activities that may affect virgin olive oil quality (1, 49). In order to obtain a characteristically fragrant and delicately flavored olive oil, it is therefore imperative that it be properly extracted from undamaged fruits at the optimum stage of ripeness (50).

Changes in chemical composition of fruit and extracted oil taking place during ripening have been studied by several authors (37, 42, 51-54). However, these deal generally with individual components and with one crop season only, whereas it has been widely demonstrated that the composition of virgin olive oil may differ significantly from one year to another (16, 17, 55).

The ratio between malic and citric acid and spectrophotometric absorption at 665 and 525 nm has been proposed as a means of determining the optimal stage for harvesting and evaluating the degree of ripeness (56), as have the changes in polyphenol content (57).

Ripeness Index. Various methods have been proposed for expressing the stage of maturity of olives. Among them, the International Olive Oil Council has suggested a simple technique based on the assessment of the color of the skin of 100 olives which are randomly drawn from 1 Kg of the sample (58). The first stage of ripening is known as the ‘green stage’, corresponding to green mature fruits that have reached their final size. Afterwards chlorophyll pigments in the olive skin are progressively replaced by anthocyanines during fruit ripening. This makes it possible to identify a ‘spotted stage’, a ‘purple
stage’ and a ‘black stage’ according to the skin color of the fruits.

**Oil content.** The oil content of the studied Cornicabra olive fruit generally increased during ripening (59). However, in some cases, where ripeness indexes were higher (>3.5-4.0), this increase was modest (as in crop season 95/96) or there was even a decrease in its value (crop 96/97). The average oil content, though varying with crop season, ranged between 35-40% of dry matter at a Ripeness Index (hereafter RI) close to 2 and 40-45% at a RI of about 4. Chimi & Atouati (57) and Gutierrez et al. (37) also observed that olive maturity significantly affects extraction yield, which increases during ripening.

**Free acidity.** An increase has been observed in free acidity as ripening progresses (59). The same behavior has been observed for Blanqueta and Arbequina (52) and Picual and Hojiblanca varieties (37). At a later stage of ripening, olives give oils with higher levels of free acidity since they undergo an increase in enzymatic activity, especially of lipolytic enzymes (60), and are more sensitive to pathogenic infections and mechanical damage.

**Peroxide value and UV absorption.** The oils obtained from olives at more advanced stages of maturity show lower peroxide values (PV), excepting only crop season 98/99 (59). This was probably due to an increase in the lipooxygenase activity. In a few cases, as in crop 95/96 and 96/97, an increase in PV was observed at an intermediate level of ripening.

$K_{270}$ also decreased at later RI in all crop seasons studied, whereas there was no clear trend of absorption at 232 nm during ripening.

**Pigments: chlorophylls and carotenoids.** The stage of olive maturity is very important for pigment, chlorophyll and carotenoid concentrations in virgin olive oil. In the early periods of olive picking, pigments were concentrated (e.g., an average chlorophyll content of 80 ppm at RI of about 2), while by the end of maturity their concentration had diminished to only a few ppm (59). The concentration of pigments correlated well with the stage of maturity of the harvested olive fruits. These results agree with the findings of other authors (37, 61).

**Oxidative stability and natural antioxidants.** In general, the values of the Rancimat stability of the Cornicabra oil decreased slightly as fruits ripened, although the trend was not linear and in some cases there was an increase at the highest RI (59). A lower oxidative stability was observed for oils of crop 95/96, due to the bad climatic conditions of previous years (16).

During ripening, the concentration of phenol compounds progressively increases until it reaches a maximum at the ‘spotted’ and ‘purple’ pigmentation stage, after which it decreases (57, 62, 63). The increase in total polyphenols at the last stage of maturity observed in the majority of the crops studied, which is responsible for the corresponding increase in oxidative stability, could be due to the reduction in water content (olive fruit humidity) observed with ripening; this can affect the extraction of partially soluble compounds (59).

The $\alpha$-tocopherol content varied slightly during ripening, and this variety exhibited no clear trend with maturity (59). Gutierrez et al. (37) have reported similar behavior for Hojiblanca, whereas for Picual, Verdial and Villalonga varieties, a clear decrease has been observed as ripening progresses (37, 52).

**Sensory analysis.** Sensory evaluation of Cornicabra virgin olive oil indicated that total scores generally diminished at higher RI (59). This was probably due to the observed loss in some positive attributes, especially fruitiness (from about 3.0 at RI close to 2, to 1.8 at RI of about 5). The bitterness score also decreased with RI, with a correlation coefficient higher than $-0.9$, with the exception of crop 98/99. The oils obtained from green olives were excessively bitter according to the panelists’ comments. As already mentioned, this does not imply rejection of the oil, but if the level of bitterness is too high it could cause problems for consumer acceptance. A high level of bitterness is a peculiar characteristic of Cornicabra virgin olive oil; but according to this study, for an optimum sensory quality of this olive oil it is recommended that the bitterness score should be lower than 4.0-3.5.

**Fatty acid composition.** Stearic acid generally increased with RI (regression coefficient $>0.8$ in many crops) and oleic acid decreased with the
stage of maturity (>0.87), with the exception of crop season 97/98 where an increase was observed. On the other hand, linoleic acid (C18:2) increased with RI in all cases, showing a good linear correlation, with a regression coefficient between 0.88 and 0.99 (59). A good linear relationship was also obtained with MUFA, PUFA and their ratio. The change in fatty acid composition with an increase of PUFA should affect the oxidative stability of olive oil, but the latter is also affected by the concentration of natural antioxidants as discussed above.

**Sterol composition.** Total sterols generally diminished slightly during ripening, with the exception of crops 97/98 where the decrease was considerable (from 1900 to 1550 ppm), and 96/97 where there was a major increase (from 1010 to 1640 ppm) (59). A decrease in total sterols has been observed by other authors (37, 64). The content in β-sitosterol generally decreases during ripening, while Δ-avenasterol increases, and the presence of desaturase activity has been suggested (37).

The change in campesterol content during ripening was not clear. In many cases, the change was minimal, and there was a slight apparent tendency to increase (as in crop 95/96) or to decrease (crop 98/99) during ripening.

**Olive oil quality and ripeness index.** To judge by the behavior of the analytical parameters studied, in particular free acidity, peroxide value, oxidative stability, sensory, oil extraction yield, and their relation to virgin olive oil quality, the best stage of maturity of Cornicabra olive fruits for processing would appear to be a ripeness index higher than 3.0 and lower than 4.0-4.5 (59).

The olive oil industry of Castilla-La Mancha mainly harvests Cornicabra olive fruits with RI greater than 5, due to popular tradition and because it is believed that the oil extraction yield always increases with maturity. It is therefore crucial to persuade these producers to bring forward the harvesting time of this olive variety in order to further improve the quality of the virgin olive oil they produce.

**INFLUENCE OF EXTRACTION SYSTEM.**

Olive oil in Spain is extracted by pressure or centrifugation systems, which vary not only in the physical forces employed to separate the oil phase but also in the amount of water used in the process. A pressure system does not require addition of water to the olive paste. However, when the olives are difficult to process and the oily phase is not easily separated from other phases, or when ripe olives are processed, it is necessary to add water to the oily must in the separation stage before it enters a vertical centrifuge. The pressure system has fallen into disuse in Castilla-La Mancha nowadays, and centrifugation is the most common procedure since large amounts of olives have to be processed in a short time. There are two centrifugation systems, the dual-phase and triple-phase decanter. In the triple-phase decanter a significant amount of water is added, and oil, residual water and solid waste are produced separately. In the dual-phase centrifugation system, no water is added, so that the system yields only oil and a plastic paste containing vegetable solids. The dual-phase decanter was introduced in Spain about ten years ago, and is now widely used because it greatly reduces liquid waste, thus helping considerably to cut down environmental pollution.

The extraction system used is critical for total phenol and o-diphenol content. However, the amounts of these compounds found in the literature differ widely due to the many variables involved in the process of extraction. The olive crushing machinery, the temperatures applied, the duration of contact with the water and the total volume of water used may all cause significant changes in the total phenol content (1, 14). Analysis of extraction system-dependent differences in the mean values of analytical determinations in the Cornicabra virgin olive oil studied revealed statistically significant differences (p<0.05) in only a few quality parameters (16, 55). For example, α-tocopherol and total phenols were greater in centrifuge-extracted oil than in pressure-extracted oil.

The α-tocopherol content in the centrifuge-extracted oil was higher than that in the pressure-extracted oil, with an Anova F-ratio value (F) of 8.3. The mean concentrations were 180, 160 and 130 mg/kg for the dual-phase,
triple-phase decanters and pressure systems respectively. Similarly, the total phenols content in the centrifuge-extracted oil was greater than that in the pressure-extracted oil (F: 4.8), with a mean content of 160, 140 and 100 mg/kg for the dual-phase, triple-phase centrifugal and pressure systems respectively. These differences in the natural antioxidants content affected the observed Rancimat stability, with mean values of 66, 57 and 46 h, respectively.

There was also a small decrease in the mean concentration of total phenols and α-tocopherol in the oils extracted using the triple-phase as compared to the dual-phase decanter, so that the latter was slightly more stable, as reported by other authors (32, 45, 65). The decrease of phenol compounds can be explained by their water solubility. Higher water/paste ratios are used in triple-phase centrifugation, and therefore larger amounts of phenols are eliminated with water wastes. However, contradictory results have been reported in some studies with respect to differences in olive oil composition due to the extraction systems employed (66, 67).

Mean contents of fatty acids and sterols differed slightly depending on the extraction system employed, although the differences were statistically significant in some cases. Palmitic, linolenic and total saturated fatty acids were statistically lower in pressure-extracted than in centrifuge-extracted oils (F: 3.3, 5.2 and 2.6 respectively), whereas oleic was higher (F: 2.0). Similarly, β-sitosterol and stigmastanol contents were lower in pressure- than in centrifuge-extracted oils (F: 3.9 and 3.1 respectively), whereas Δ5,24-stigmastadienol, Δ5-avenasterol and apparent β-sitosterol were higher (F: 7.1, 3.8 and 3.2 respectively).

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