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Influence of olive crushing temperature on phenols in olive oils

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Abstract An experimental investigation was carried out to evaluate the influence the different temperatures at which olives are hammer-crushed and paste kneaded had on the quality of oil and particularly on the phenolic components. The results obtained showed that temperature influenced the diffusion of phenolic compounds in oil. Greater amounts of hydroxytyrosol, tyrosol, caffeic acid, hydroxycaffeic acid and oleuropeine were measured in oils obtained from previously refrigerated olives. Kneading brought about a reduction of total phenols when it was performed on olives crushed at a higher temperature (18 °C) while it led to a slight increase when it was executed on pastes of previously refrigerated olives (6 °C).

Keywords Olive oil · Olive crushing · Phenols · Influence of temperature

Introduction

Phenols represent the class of compounds which mainly confers the organoleptic properties and resistance to oxidation of virgin olive oils while also contributing to determine some of their nutritional characteristics [1–6].

The amount of phenols present in virgin olive oils depends on the way the olive paste is prepared. Previous papers have highlighted that using a hammer-crusher rather than a stone-mill produces a greater content of total phenols while kneading of the paste generally leads to their reduction [7–10]. The greater amount of total phenols present in the oils obtained from a hammer-crushed paste as compared to the oils extracted from milled pastes may be ascribed to the higher temperatures reached during crushing as well as to a greater activation of solubilization phenomena by which more phenolic compounds pass from their structural sites into the oil [11]. In addition, the paste temperature rises substantially during rapid crushing of the drupes due to the friction of the paste against the grid and hammer surfaces before being removed from the crusher. This inevitably has an impact on the quality of the oils and on the phenolic components in particular.

The aim of this paper is to assess the influence of the input temperature of the olives when they are fed into the crusher and of paste kneading on the quality of the oil obtained by focusing especially on the phenols present. For this purpose, homogeneous batches of olives were hammer-crushed at different temperatures and then kneaded. In all the cases processing procedures were executed irrespective of the effects they could have on the oil yields.

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Materials and methods

Sample preparation

Five different batches of olives picked by hand during the optimal stage of ripening were considered for the experiments. After washing and leaf-removal, each batch was divided in two homogeneous portions and conditioned at 18 °C and 6 °C, respectively. The hammer-crushing and the kneading processes were carried out utilizing a pilot plant [8]. Homogeneous samples of paste of at least 5 kg were then collected from each group of olives and the oil was extracted by means of a laboratory basket centrifuge. All the oil samples were filtered through cotton before being analyzed. The flux diagram of the processing procedures are shown in Fig. 1.

Routine analysis

The titratable acidity, the peroxide value, and the coefficient of specific extinction at 232 and 270 nm (K_{232} and K_{270}) were deter-

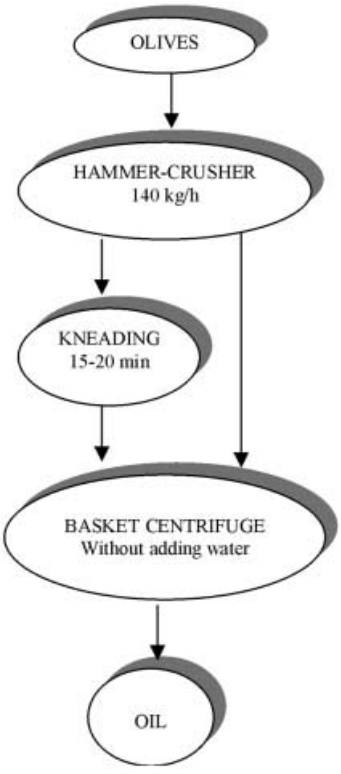

Fig. 1 Flux diagram of the processing procedures

mined for each oil sample according to the EC Regulation no. 2568/91 [12].

Phenolic compounds determination

The total phenolic compounds of the virgin olive oils were determined according to the method described by Caponio et al. [7]. Qualitative and quantitative evaluations of phenolic compounds were carried out by analyzing the phenolic extracts with HPLC using gallic acid as an internal standard. The HPLC system was composed of a Beckman chromatograph equipped with a 250 mm × 4.6 mm C_{18} Ultrasphere-ODS column; the eluates were detected at 278 nm. The mobile phase used was 2% acetic acid in water (A) vs. methanol (B). The elution gradient applied at a flow rate of 1 ml/min was: 95% A/5% B for 3 min, 80% A/20% B in 15 min, and isocratic for 2 min, 60% A/40% B in 10 min, 50% A/50% B in 10 min, 100% B in 10 min until the end of the run. Samples were dissolved in methanol, and 10 μl of this solution were injected into the column. The standards used and the quantitative assessment of each compounds of interest were carried out as described elsewhere [7]. The peaks were identified by comparing the retention time of each peak with that of the corresponding standard. The peaks that were more difficult to identify were verified by adding the corresponding standard. In all the sample examined, six unidentified peaks were also present. According to the literature, they are believed to correspond to at least six phenolic compounds [13–14]. The repeatability of the method employed was found to be 7%, as determined by several analysis carried out on the same sample.

Auto-oxidation stability

The resistance to auto-oxidation of the oils was evaluated using the Rancimat system (Methrohm Co.) at 120 °C with an air flow of 20 l/h. The results were expressed as induction time (hours).

Results and discussion

Tables 1 and 2 contain the mean analytical values obtained for the oils extracted from drupes at different temperatures as well as the mean analytical composition of the individual phenolic compounds.

The mean values obtained in the routine analyses (Table 1) were slightly lower in the oils extracted from drupes processed at a lower temperature. In all the cases paste kneading led to slight increases in the parameters considered. The values obtained, however, were such that all the oils could be classified as extra virgin olive oils [12].

On average, the total phenols (Table 1) were about 40% greater in the oils obtained from the olives crushed at the highest temperature (18 °C). This finding would seem to suggest that the temperature at which olives are processed should be considered as one of the factors responsible for the greater diffusion of phenolic compounds in an oil. As a result of the amount of total phenols present, also the induction time of the oils, as determined by the Rancimat method, was on average 20% greater in the oils extracted from the olives processed at the highest temperature. This further demonstrates the significant correlation that had already been reported to exist between the amount of total phenols and induction times [7, 8]. Paste kneading led to a reduction in the total phenol content in the oils obtained

Table 1 Characteristics of the extra virgin olive oils extracted from drupes at different temperatures

Analyses	Olives at 18 °C		Olives at 6 °C	
	C[a]	C+K	C	C+K
Free fatty acids [%]	0.31 (0.03)	0.33 (0.03)	0.30 (0.02)	0.31 (0.02)
Peroxide values [meq/kg]	3.9 (0.4)	4.2 (0.3)	3.6 (0.3)	3.8 (0.2)
K_{232}	1.646 (0.040)	1.687 (0.027)	1.633 (0.023)	1.643 (0.043)
K_{270}	0.173 (0.011)	0.185 (0.013)	0.167 (0.008)	0.172 (0.012)
Total phenols [mg/kg]	453 (45)	403 (51)	329 (43)	357 (37)
Induction time [h at 120 °C]	14.6 (1.1)	14.2 (0.9)	12.1 (1.3)	12.4 (1.3)

[a] $n = 5$; mean and standard deviation (in parentheses)
Abbreviation: C = crusher; K = kneader

Table 2 Phenolic compounds (mg/kg) of the extra virgin olive oils extracted from drupes at different temperatures

Analyses	Olives at 18 °C		Olives at 6 °C	
	C[a]	C+K	C	C+K
fraction 1				
Hydroxytyrosol	0.76 (0.12)	0.83 (0.21)	2.49 (0.43)	2.31 (0.45)
Tyrosol	1.55 (0.49)	2.06 (0.49)	3.63 (0.54)	3.35 (0.65)
Hydroxycaffeic acid	0.03 (0.01)	0.03 (0.01)	0.20 (0.07)	0.05 (0.01)
Vanillic acid	0.52 (0.08)	0.54 (0.09)	0.38 (0.12)	0.40 (0.12)
Caffeic acid	0.04 (0.02)	0.04 (0.01)	0.22 (0.05)	0.07 (0.02)
Syringic acid	0.20 (0.07)	0.22 (0.04)	0.13 (0.07)	0.13 (0.06)
p-Coumaric acid	0.42 (0.12)	0.34 (0.09)	0.24 (0.08)	0.18 (0.09)
Ferulic acid	0.60 (0.18)	0.42 (0.12)	0.39 (0.07)	0.37 (0.12)
Cinnamic acid	0.32 (0.16)	0.35 (0.12)	0.22 (0.06)	0.22 (0.05)
Total fraction 1	*4.45 (0.74)*	*4.83 (0.77)*	*7.89 (0.46)*	*7.07 (1.19)*
fraction 2				
Peak I (RT 38.3)	79.68 (6.17)	74.80 (6.91)	65.23 (4.97)	66.22 (4.56)
Peak II (RT 39.5)	43.50 (7.29)	32.46 (9.03)	29.72 (4.30)	26.37 (7.97)
Oleuropeine	4.31 (1.47)	3.27 (1.43)	8.16 (2.03)	6.34 (1.46)
Peak III (RT 42.7)	76.65 (5.95)	73.98 (6.80)	62.42 (6.44)	59.28 (3.96)
Peak IV (RT 43.6)	34.40 (2.91)	25.61 (6.18)	27.08 (7.76)	24.27 (6.20)
Peak V (RT 46.5)	8.68 (1.89)	8.97 (1.18)	4.54 (2.09)	4.57 (2.13)
Oleuropeine aglycone	27.95 (5.84)	26.00 (6.53)	24.15 (5.77)	21.58 (6.36)
Apigenin	20.46 (4.33)	20.26 (3.94)	20.04 (4.38)	16.09 (3.32)
Peak VI (RT 50.7)	17.04 (1.23)	14.26 (2.34)	11.28 (1.83)	10.86 (2.71)
Total fraction 2	*312.68 (31.99)*	*279.60 (32.27)*	*252.63 (27.01)*	*235.59 (18.70)*

[a] $n=5$; mean and standard deviation (in parentheses)
Abbreviation: C = crusher; K = kneader

from olives processed at 18 °C while a slight increase was registered in the oils extracted from drupes processed at 6 °C. The variations occurring in phenolic compounds during kneading may be ascribed to the rise in temperature which influences the chemical and physical properties of the water/oil colloidal system; they may also arise from a set of contrasting, temperature-related mechanisms that are probably caused both by solubilization and hydrolysis leading to the passing of these substances from their structural sites into the oil and by oxidative phenomena taking place in the phenols that solubilized during the oily phase [11, 15]. As a result, when olives refrigerated at 6 °C were processed, even the induction times of the oils obtained from hammer-crushed and kneaded pastes were longer than the times registered for the oils extracted from the pastes that had only been hammer-crushed.

The individual phenolic compounds (Table 2) have been grouped together in two discrete fractions: fraction 1 comprising simple phenols and fraction 2 consisting of hydrolyzable phenols and unknown peaks corresponding to complex phenols.

In the oils obtained from olives hammer-crushed at 6 °C, the whole of fraction 1 was almost twofold the amount measured in the oils extracted from olives processed at 18 °C, with mean values of 7.89 and 4.45 mg/kg, respectively. These greater quantities are to be mainly ascribed to the greater amounts of tyrosol and hydroxytyrosol measured in the oils extracted from the olives processed at a lower temperature, which also proved to contain greater amounts of caffeic and hydroxycaffeic acids as shown in Fig. 2. The other simple phenols were generally present in greater quantities in the oils extracted from the olives processed at a higher temperature. This overall situation may be due to oxidative phenomena that occurred in greater amounts in oils extracted from olive crushed at higher temperature and which affect the free phenols solubilized in the oily phase after instantaneous heating of the olive paste during crushing.

The whole of fraction 2, instead, was more abundant in the oils obtained from the olives crushed at a higher

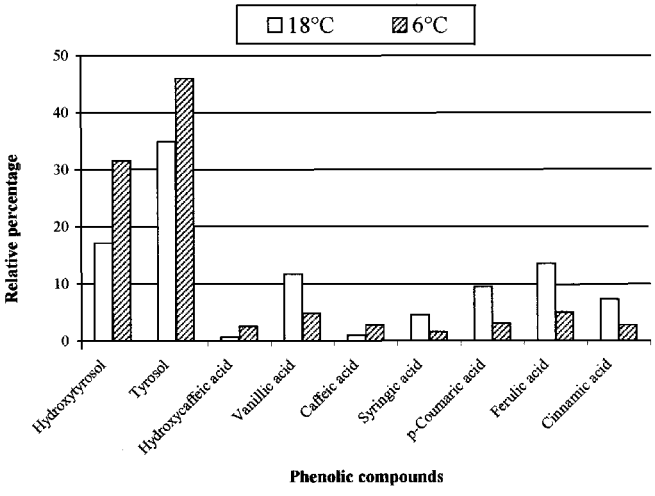

Fig. 2 Relative percentage of simple phenolic compounds grouped in fraction 1

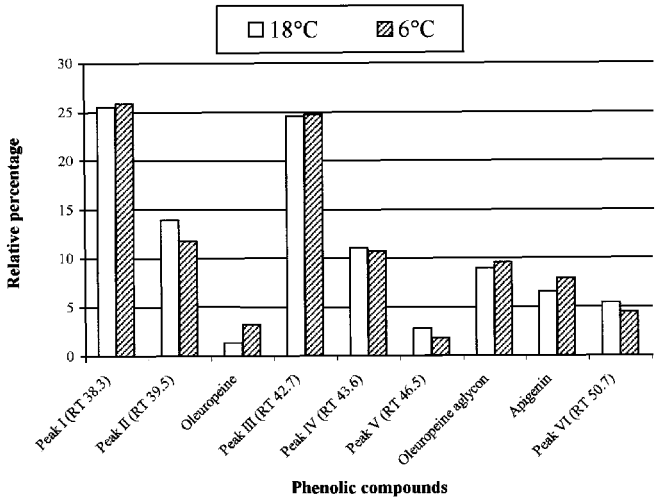

Fig. 3 Relative percentage of individual phenolic compounds grouped in fraction 2

temperature, with mean values of 312.68 and 252.63 mg/kg in the oils extracted from the olives processed at 18 °C and 6 °C, respectively. However, as shown in Fig. 3, the individual phenolic constituents did not register substantial percent changes compared to the total of fraction 2 in the oils extracted from olives processed at different temperatures. Amongst the constituents of this fraction, oleuropeine is present in greater amounts in the oils extracted from olives processed at 6 °C and this may be ascribed to the fact that oleuropeine degradation is reduced due to the lower activity of β-glucosidase during crushing [16, 17].

With the exception of a few individual phenolic compounds, all the others were observed to decrease in the oils obtained from drupes processed at both 18 °C and 6 °C when the olive paste was kneaded. This decrement may be ascribed to the activity of lipoxygenase which is released during crushing and is not inactivated during kneading, as well as to the interchange between water and oil fostered by the colloidal complex of the pastes [17].

Conclusions

The results observed lead to the following considerations:

- the temperature at which olives were processed influenced the diffusion of phenols in oil,
- the oils obtained from olives crushed at 6 °C contained greater amounts of tyrosol, hydroxytyrosol, caffeic acid, hydroxycaffeic acid, and oleuropeine,
- paste kneading led to a reduction in the amount of total phenols in the oils obtained from olives processed at room temperature while a slight increase was observed in the oils extracted from cooled drupes, probably due to the low temperature which influences the chemical-physical properties of olive pastes,
- kneading of the paste generally led to a slight decrease of individual phenolic substances present in oil,
- fraction 2 consisted of hydrolyzable phenols and was present in greater quantities than fraction 1 (simple phenols); it may therefore be more responsible for the protection of the oils.

Finally, in order to establish optimal parameters for processing procedures, further knowledge should be attained concerning the influence the temperature at which olives are crushed has on the quality of extra virgin olive oil without disregarding the anti-oxidants and pro-oxidants which seem to be involved in the process of oil extraction.

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