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Changes in the Biochemical Composition of the Tataouine Virgin Olive Oils During Thermal Oxidation

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Abstract: An experimental investigation was carried out to evaluate the quality of virgin olive oils from varieties (Chemlali Tataouine, Fakhari Douirat, Zarrazi Douirat, and Dhokar Douirat) grown in the harsh conditions of the arid region of Tataouine, using accelerated oxidation and deep frying studies at 180 ˚C from 0 to 10h. The experimental data showed the resistance of the studied oils to the oxidation especially Chemlali Tataouine and Zarrazi Douirat who maintained their high stability and their natural biophenol contents during 2.5 and 5h, respectively, under frying temperature. A positive correlation was observed between the induction time and the total polar phenol contents during the thermal oxidation. The capacity of the heated and unheated oils to quench the free radicals has been also studied.

Keywords: Antioxidant, Frying, Oxidation, Virgin olive oil

1. Introduction

Recent studies suggest that the phenolic compounds naturally contained in virgin olive oil (VOO) improve its resistance to oxidative deterioration (Gordon *et al*., 2001). In fact, they interrupt the initiation and propagation stages of the oxidative chain reaction since they act as chain breakers by donating a radical hydrogen to alkylperoxyl radicals formed during the propagation step of lipid oxidation and subsequently forming a stable radical ($A^{\bullet}$) through the well-known reaction (Frankel, 1998): $ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$, and therefore improve the oxidative stability of virgin olive oil and extend its shelf life. In southern Tunisia, the region of Tataouine (latitude 32˚55′ north; longitude 10˚09′ east) is Characterized by a harsh pedoclimatic conditions (chalky grounds, low rainfall (88-157 mm year^{-1}) and a high temperature (max 45 ˚C). Despite these severe conditions, the cultivation of the olive tree being the principle agricultural commodity in this region. In fact, because of the lack of rainfall and the limited resources of underground water, growing takes place in depressions to obtain the maximum of water. In this region, there are some virgin olive oils from autochthonous varieties who showed an excellent natural antioxidant composition (Oueslati *et al*., 2009). To discover the degree of protection of such compounds to the oils and to better understand how the quality of olive oil is affected over time, an accelerate thermal oxidation of VOOs has been done at deep-frying temperature. So, the aim of this study was to establish the chemical changes occurring in the VOOs from Tataouine varieties after exposure to high temperature (180˚C).

2. Materials and Methods

2.1. Oil samples

Four samples of VOOs were analysed from the following varieties: Chemlali Tataouine (CHt), Fakhari Douirat (FD), Zarrazi Douirat (ZD), and Dhokar Douirat (DD). All the varieties were grown in the locality of Douirat in the region of Tataouine (southern Tunisia). Oil extraction was performed using an Abencor laboratory oil mill, kneading the olive paste at 28˚C for 30 min. All samples were stored in the freezer in darkness in amber glass bottles until analysis. A comparison with the main Tunisian variety Chemlali (CH), grown in the region of Sfax (35˚00'N; 10˚33'E; 128 m asl; ~ 230mm rain year^{-1}; mean temperatures: 15-29 ˚C, slightly alkaline sandy soil (pH ~7.5)), was also carried out.

2.2. Heating experiment

From the oil samples, 70g was placed into 100mL open glass beakers (7 cm high, 5 cm i.d.). The

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beakers were heated at 180 ˚C for 10h in an oven. Aliquots of the heated oils (10 g) were taken every 2.5 h and stored at -20˚C in sealed dark glass vials under nitrogen atmosphere until analysis.

2.3. Determination of induction time

Induction time was evaluated by the Rancimat apparatus (model 743, Metrohm Co., Basel, Switzerland). Stability was expressed as the oxidation induction time (h) using 3.5g of oil. The temperature was set at 100 ˚C, and the air flow rate was 10 L h^{-1}.

2.4. Colorimetric determination of total phenolics content

Total phenols were measured in the polar fraction extracted from 2.5 g of oil using methanol/water (60:40 v/v), and the determination was based on the Folin-Ciocalteu method (Tsimidou, 1998). Results were expressed as caffeic acid (CA) equivalents (mg CA kg^{-1} oil).

2.5. Antioxidant capacity (AOC) of the VOO samples

The olive oil samples were analyzed for their capacity to scavenge the stable 1,1-diphenyl-2-picrylhydrazyl radical ($DPPH^{\bullet}$) using the method of Kalantzakis *et al.* (2006**)** .

3. Results and Discussion

The induction time of the unheated oils, showed wide variation among the different tested VOOs (**Fig. 1**). The oil stabilities ranged from a minimum of 30h for Dhokar Douirat to 100h for Chemlali Tataouine. According to these results, the olive varieties used in this study could be considered representative examples of low- and high-stability olive oils. In accordance with the overall mechanism proposed for the autoxidation process and the induction time calculated for the VOO samples, we can differentiate two groups of oils. The more stable VOOs are Chemlali Tataouine, Zarrazi Douirat and Fakhari Douirat with an induction time of 100, 83 and 63 h, respectively, whereas the less stable oils are Dhokar Douirat which showed an induction time (30h) similar to that of Chemlali (34h). As shown in figure 1, the induction time of Chemlali, Fakhari Douirat and Dhokar Douirat decreased rapidly by 43, 34 and 27%, respectively during 2.5 h of heating at 180 ˚C. Whereas, Zarrazi Douirat maintained its induction time during 2.5 h of heating. Except the VOO of Chemlali Tataouine, a drastic decrease in the induction time in all the remaining varieties after 2.5 h of heating. These results are similar to those found in the heated VOOs from Spanish varieties Picual and Cornicabra which are the most stable oils (Salvador *et al*., 2001).

Concerning Chemlali Tataouine VOO, it is interesting to underline its very high capacity to maintain its induction time during 5 h. In fact, there are considerable changes in the induction time of its unheated and heated VOO (100-84 h, respectively) during 5 h. Chemlali Tataouine VOO showed a decrease by 50% in its induction time at 7.5 h of heating and maintained this stability, which is considered high (>50 h), for a long period, even after 10 h of heating. This exceptional potential may be due to the conjunction of high phenol content and high levels of monounsaturated fatty acids in such variety (Oueslati *et al*., 2009).

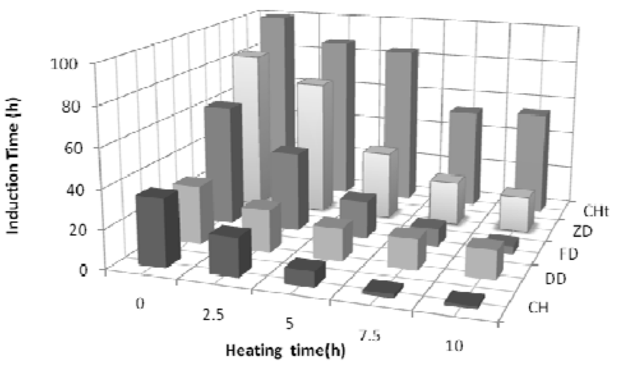

Fig. 1. Change in the induction time of the Tataouine VOOs during heating at 180 ˚C as compared to Chemlali VOO with CHt, Chemlali Tataouine; ZD, Zarrazi Douirat; FD, Fakhari Douirat; DD, Dhokar Douirat and CH, Chemlali.

The results given in **figure 2** indicate that the unheated VOOs of Chemlali Tataouine, Zarrazi Douirat and Fakhari Douirat are with remarkable high contents of total polar phenols (> 450 mg CA kg^{-1}). Chemlali Tataouine showed the highest total polar phenols with an amount reaching 802 mg kg^{-1}. Whereas, Dhokar Douirat and Chemlali are with the lowest total polar phenol contents (< 400 mg CA kg^{-1}). During the heating, the total polar phenol content of Dhokar Douirat VOO declined drastically by 78% after 2.5 h of heating at 180 ˚C. This result is in agreement with that reported by Gómez-Alonso *et al.* (2002), who found that the concentration of hydroxytyrosol and its secoiridoid derivatives of a VOO sample decreased after 2.5 h of heating at 180 ˚C. In opposite, all the remaining studied samples, although they showed a diminution by 50% in their total polar phenol content after 2.5 h of heating, they showed a relatively high phenol content (173-400 mg kg^{-1}). It is interesting to mention that Chemlali Tataouine showed a high polar phenol content (> 372 mg CA kg^{-1}) even after 5 h of heating.

A correlation between polar phenol compounds and the induction time is well-established in the cases of unheated and heated oils ($R^2 > 0.8$) (**Fig. 3A**). Dhokar Douirat VOO, which had the lowest total polar phenol content, showed the lowest oxidative stability, whereas, Chemlali Tataouine which showed the highest total polar phenol content, showed the highest induction time.

It can be seen from the results of **figure 4** that the AOC of unheated Chemlali Tataouine, Zarrazi Douirat and Dhokar Douirat virgin olive samples were similar and higher than those of unheated VOOs of Fakhari Douirat and Chemlali, probably due to the much lower tocopherol content of the latter oils (Oueslati *et al*, 2009). Fakhari Douirat and Chemlali VOO samples practically lost their AOC after 2.5 h of heating at 180 ˚C. The other studied samples seemed to maintain some of their AOC for a longer period, even after 10h of heating. It is interesting to stress that Chemlali Tataouine showed the highest AOC during heating, in fact, it maintain all its capacity to scavenge the free radicals during 5 h of heating;

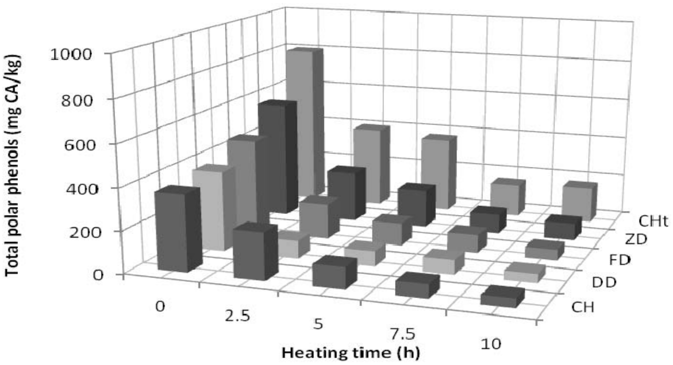

Fig. 2. Change in the total polar phenol contents of the Tataouine VOOs during heating at 180°C as compared to Chemlali VOO with CHt, Chemlali Tataouine; ZD, Zarrazi Douirat; FD, Fakhari Douirat; DD, Dhokar Douirat and CH, Chemlali.

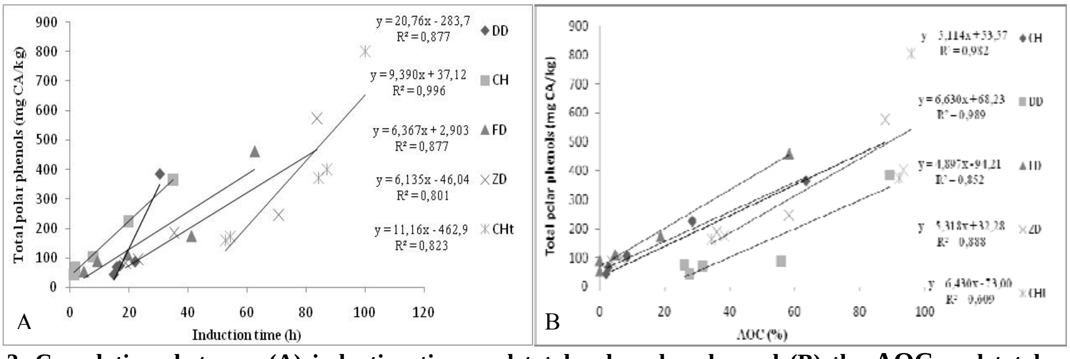

Fig. 3. Correlations between (A) induction time and total polar phenols, and (B) the AOC and total polar phenols during heating of the studied VOOs with CHt, Chemlali Tataouine; ZD, Zarrazi Douirat; FD, Fakhari Douirat; DD, Dhokar Douirat and CH, Chemlali.

at 7.5 h of heating it lost 65% of its capacity to scavenge the free radical [DPPH•]. The capacity of Chemlali Tataouine VOO to quench the free radicals is much more higher than that found in heated Greek and Spanish virgin olive oils (Kalantzakis *et al.*, 2006**)**. Practically, Chemlali Tataouine and Dhokar Douirat maintained about 30% of their AOC after 10 h of heating. This may be due to their highest initial total tocopherol content (Oueslati *et al.*, 2009) and total polar phenol content. But except the oil of Chemlali Tataouine, good correlations were observed between the AOC and the total polar phenols in all the remaining studied oils with $R^2 > 0.850$. In Chemlali Tataouine, although the phenol content showed a decrease in the three first times of heating (0-5 h), the AOC was maintained. This fact may be due to the high contribution of the tocopherols by comparison with that of the phenols in the AOC of such variety and as a consequence, the correlation between the AOC and the total polar phenols is not very high ($R^2 > 0.609$) (**Fig. 3B**).

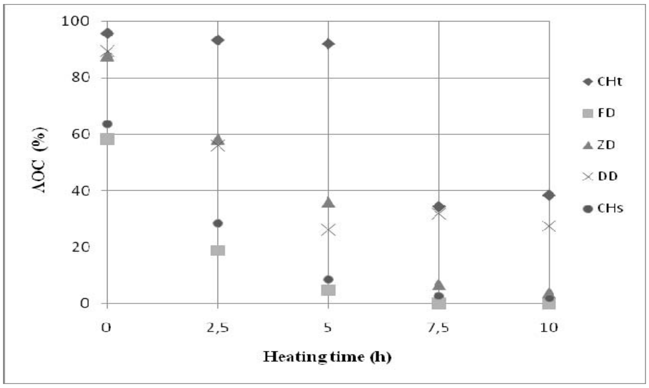

Fig. 4. Change in the antioxidant capacity (AOC) of the Tataouine VOOs during heating at 180°C as compared to Chemlali VOO with CHt, Chemlali Tataouine; ZD, Zarrazi Douirat; FD, Fakhari Douirat; DD, Dhokar Douirat and CHs, Chemlali.

4. Conclusions

According to the literature, VOO rapidly losses its valuable natural antioxidants (polar phenols and α-tocopherol) during heating (Brenes *et al.*, 2002) or in the early stages of frying of potatoes (Andrikopoulos *et al.*, 2002), although it keeps its thermal stability for a longer time. These results should be taken into consideration when VOO is recommended for frying. But, in the case of Zarrazi Douirat and especially Chemlali Tataouine, this study showed their high potential when they are recommended for frying. These oils have a remarkable stability, total phenol contents and as a consequence high AOC at frying temperatures.

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