



Effects of sunlight, temperature and adulteration on the quality of the virgin olive oil

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Abstract

The Moroccan Picholine olive variety shows performance against climate stress and environmental constraints. The virgin olive oil is exposed to extraction conditions, storage and commercialization that could alter its quality. Among the factors involved by these conditions there are; sunlight, temperature and adulteration. The objective of the present work was to evaluate the impact of such factors on the quality of the virgin olive oil extracted from the Moroccan Picholine variety. So, we have determined characteristic parameters of the quality of the virgin olive oil (VOO) like water content (WC), peroxide index (PI), acid index (AI) and density (D) according to sunlight, temperature and adulteration effects. 25 samples of VOO from the «Moroccan Picholine» cultivar in two areas in Morocco (Demnat Virgin Olive Oil and Tagzirt Virgin Olive Oil) have been studied using chemical analytical methods and pycnometry. VOO from the two Moroccan areas (DVOO and TVOO) presents low peroxide index when it is stored 15 days in obscurity. Concerning water content (WC), peroxide index (PI), acid index (AI) and density (D) parameters, a similar behavior has been observed between the two virgin olive oils (VOOs). The evolution of oils according to temperature was also evaluated. The samples were slowly heated until the temperatures of 25, 40, 55, and 70 °C. For, each VOO sample, each one of these four temperatures was maintained 10 mn. The same analyses were carried out on VOO adulterated by Refined Olive Oil (ROO). The sunlight promotes oxidation in DVOO and TVOO so that the PI Index increased but has no significant effect on the AI and the density. The WC at 25°C in TVOO is greater than the one in DVOO. In the case of heated oil, water content in DVOO, TVOO and ROO decreases progressively with temperature. The olive oil stored in darkness is affected by temperature since it makes the PI increasing from 14.6 to 19.9 O₂ meq/kg in TVOO and from 16.9 to 19.9 O₂ meq/kg in DVOO. DVOO and TVOO present a considerable decreasing of PI when they are adulterated by ROO. AI values of TVOO are higher than those of DVOO and decrease after adding ROO, especially below 10% of ROO. Heating makes AI increasing in oils and the heated oil the greatest AI is TVOO. A consistent result has been recorded in the case of the sunlight effect on the value of AI in TVOO whose acid index was 0.51% in the darkness and 0.73% at sunlight. Globally, virgin olive oil density increases according to the temperature and to the adulteration by refined olive oil.

Keywords: Virgin olive oil, sunlight, temperature, adulteration, acidity, peroxide index.

1. Introduction

Olive oil, known for its health properties as a Mediterranean food is still studied by the scientific community. It contains antioxidant substances that the therapeutic effect has been proved [1-3]. Cultivar, geographic site, irrigation, climate, soil and olive collecting conditions are influencing factors of the quality of olive oil [4-9]. Moreover, oil extraction conditions are determining on the quality [10], namely on acidity and oxidizability [11]. In the virgin olive oil (VOO) that was heated at 190 °C in a discontinuous industrial fryer for 40 hours, the evolution during heating of the acyl group proportions and of the iodine value was monitored by 1H nuclear magnetic resonance. Monounsaturated acyl groups degraded at faster rates than linoleic and linolenic groups. The formation of primary oxidation compounds was not observed with this technique [12]. Exposure of olive oil samples to light and temperatures (35 °C) caused substantial deterioration of the quality parameters [13]. Partial least squares (PLS) was coupled to Raman spectroscopy of VOO collected samples at eight different temperatures from 20 to 90 °C so that a strategy of the Raman spectroscopy accuracy was further evaluated for

the identification of soybean oil-adulterated olive oils using linear discriminant analysis (LDA) [14]. In Morocco a study has been, recently, undertaken on phenolic compounds to valorize Picholine cultivar but there is still a need of studies on the performances of the Moroccan Picholine olive cultivar that presents fungicide effects among other valorizing characteristics [15]. The present work aims to contribute to remedy such lack in the valorization of the Moroccan Picholine olive cultivar.

2. Materials and methods

Olive oil samples were collected in "Demnat" and "Tagzirt" geographic zones in the Moroccan "Tadla-Azilal" area between November 2010 and March 2011. All samples have been submitted to mechanical press. 25 virgin olive oil samples, 13 from Tagzirt and 12 from Demnat, extracted from "Moroccan Picholine" olive cultivar were obtained and stored one month in a temperature of 15°C, in darkness, before analysis. Water content (WC) in virgin olive oils (VOOs) was determined by using the Karl Fisher method (Titrator Mettler Toledo DL38). Peroxide index (PI) was obtained by volumetric titration using oxido-reduction reaction between sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, Riedel-de Häen: purity > 99.8%) [16] and oil peroxide [16]. Thanks to volumetric titration, acid index (AI) was measured by potassium hydroxide (KOH, Riedel-de Häen: purity 99.8%) [16]. Determination of density (D) was conducted by using the 25 mL Guy Lussac pycnometers [16]. Sunlight effect at 25 °C has been evaluated by comparing WC, PI, AI and density of the oil in darkness to those parameters obtained when the oil samples were exposed 15 days to sunlight. The evolution of oils according to temperature was also evaluated. The samples were slowly heated until the temperatures of 25, 40, 55, and 70 °C. For, each VOO sample, each one of these four temperatures was maintained 10 mn. The same analyses were carried out on VOO adulterated by refined olive oil (ROO).

3. Results and discussion

3.1. Sunlight effect

The values of the quality parameters of Demnat VOO (DVOO) and Tagzirt VOO (TVOO) samples when exposed to sunlight are presented in table 1.

Table 1: Parameters of the quality of DVOO and TVOO exposed to sunlight at 25°C. WC: water content, PI: peroxide index, AI: acid index, D: density

Sample	WC (%)	PI (O_2 m.eq/Kg)	AI (%)	D
DVOO	0.26	24	0.70	0.90
TVOO	0.59	21.2	0.73	0.88

3.2. Heating and adulteration effects

The figure 1 presents the effects of the temperature on Tagzirt Virgin Olive Oil (TVOO), Demnat Virgin Olive Oil (DVOO) and Refined Olive Oil (ROO) parameters after having stored oils in darkness at 10°C.

The Figure 2 presents the effects of the adulteration by ROO, on the quality parameters of TVOO and DVOO, after having stored oils in darkness at 10°C.

3.3. Sunlight effect at 25°C

As we can observe in table 1 and after the international olive oil council (IOOC), WC values in DVOO and TVOO samples that were exposed to sunlight, at 25°C, are not matching to the IOOC standards [16]. Contrarily to AI values in the two VOOs, the PI values in VOOs do not correspond to these IOOC standards. The density values are, globally, less than those of the codex olive oils standard. The sunlight promotes oxidation in DVOO and TVOO so that the PI Index increases but it has no significant effect on the AI and the density. However, after Orlandi F. and al. [17] unsaturated fatty acids, when they are in a matrix like olive wood, could be oxidized by the sunlight. It has been reported in their work that evaporation of the volatiles caused by sunlight has a great effect on an acidity quality of the oil [17].

3.4. Water content

3.4.1: In olive oil at 25 °C

The table 1 shows that the WC in TVOO is greater than the one in DVOO. The principal causes of WC increasing in non-refined VOO are due to the extraction process in a case of traditional mill in which the separation of water-oil mixture is realized by simple difference between the density of the oil phase and the aqueous one. In fact, this difference is sufficient for decanting of the aqueous phase except in case of the stabilization of the "olive oil- water" emulsion [18].

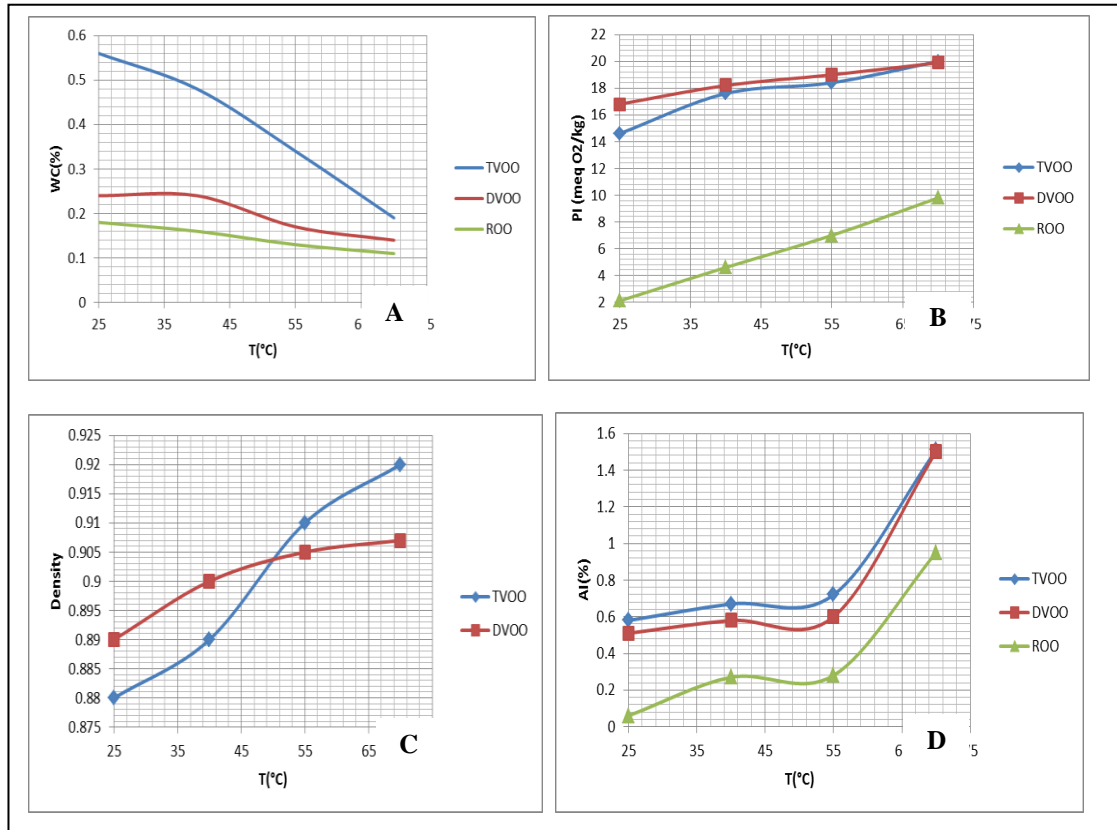


Fig.1: Temperature effects on the quality parameters of TVOO, DVOO and ROO, after having stored oils in darkness at 10°C: 1.A: WC, 1.B: PI, 1.C: Density and 1.D: AI.

3.2.2: In heated oil

Also, the figure 1.A shows that water content in DVOO, TVOO and ROO decreases progressively with temperature. The decreasing of WC in the three heated oils, according to heating, can be explained by the fact that the temperature increasing allows increasing of the pressure of the oil vapor, so that it leads to the transformation of water molecules and volatile compounds from the liquid state to the gaseous one. WC must be minimized in all olive oils to decrease water activity (WA) and consequently to reduce the proliferation speed of micro-organisms that cause olive oil damage [19-22].

3.4. Peroxide Index

3.4.1 : In heated olive oil

As it is observed in figure 1.B, the quality of the olive oil after having stored it in darkness is affected by temperature. When it increases from 25 to 75°C, PI increases, too, from 14.6 to 19.9 O₂ meq/kg in TVOO and from 16.9 to 19.9 O₂ meq/kg, in DVOO. So, the PI value increases relatively slightly without curve breaking, contrarily to the curves of density (figure 1.C) and AI (figure 1.D), as we will see hereafter. A temperature increasing accelerates lipids oxidation by promoting peroxides (figure 1.B). Catalyzed oil auto-oxidation by temperature is susceptible to yield a damage of its biochemical, organoleptic and nutritional characteristics. Such damage of edible oils by temperature is known in hot seasons where temperatures exceed 40°C in some geographic sites presenting continental climate and olive oil production like the two areas in where we collected the samples. The refined olive oil PI values are lower than those of DVOO and TVOO. They were rising from 2.1 to 9.8 meq/kg of O₂, from 25°C to 75 °C. The increasing of temperature induces the mechanism of fatty acids damage, promotes peroxides accumulation and damages phenolic compounds that are anti-oxidants in olive oil [12, 22, 23]. So the olive mills in where we extracted VOO should produce oils presenting PI respecting IOOC standards. In fact, these mills have assured extraction conditions like olives washing that minimize metallic catalysts of oxidation and reduction of grinding time while the oil is exposed to free air. Furthermore, the conservation of samples at a temperature below 17°C has also allowed us to save the quality of the olive oils.

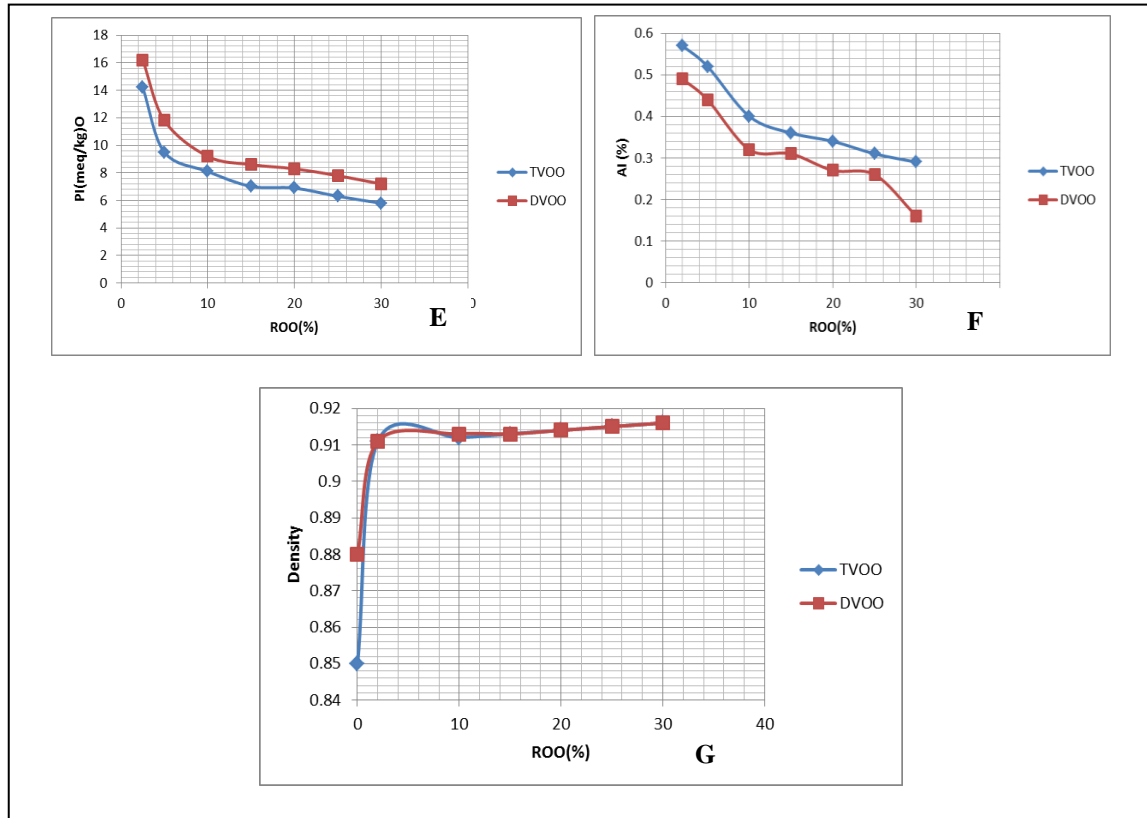


Fig.2: Adulteration effects on the quality parameters of TVOO and DVOO, after having stored oils in darkness at 10°C: 2.E: PI, 2.F: AI and 2.G: Density.

3.4.2: In adulterated oil

According to figure 2.E, DVOO and TVOO show a considerable decreasing of PI when ROO is added, particularly below 5% as a percentage of the adulteration. This result was expected since refining should make VOO presenting a less PI. Values of PI in adulterated oil samples are still in accordance with the standards [16]. So, a quality control can't easily detect an adulteration of VOO by ROO by only a simple checking of PI.

3.5. Acid index

3.5.1: In adulterated oil

Figure 2.F shows that AI values of TVOO are higher than those of DVOO. AI of the two VOOs decreases, after adding ROO, especially below 10% of ROO. Such a decreasing of AI in VOO adulterated by ROO can be explained by the low acidity of the refined oil [24, 25]. So, the refining should make stabilizing the free acidity of olive oil.

3.5.2: In heated olive oil

Globally, heating makes increasing AI in oils and the greatest AI in heated oil was in case of TVOO (figure 1.D). A consistent result has been recorded in the case of the sunlight effect on the value of AI in TVOO whose acid index was 0.73% (table 1) at sunlight and 0.51% in the darkness. AI values of ROO are inferior to those in DVOO and TVOO (figure 1.D). This explains that one of the refining aims is to stabilize oil acidity. So an olive oil adulteration by ROO allows decreasing acid index. Above temperatures of about 63°C (figure 1.D) DVOO and TVOO, as virgin oils, do not present AI values inferior than 1% in oleic acid terms [16], contrarily to ROO. Temperature increasing seems to affect the triglycerides in the three oils, liberating fatty acids. Consequently, these heated oils sustain a relative increasing acidity and oxidation. This result confirms the one of previous works on the effect of heat stress on olive oil quality [26-28].

3.6. Density and adulteration

It can be observed in figure 1.C, when the temperature does not exceed 47 °C, that DVOO is slightly denser than TVOO. Globally, it seems that the temperature makes increasing the density of the oils, slightly. Such

increasing of the density is not easy to be highlighted as one can think. A first explanation of this result would be that, in the microscopic level, water and volatile compounds are removed from the liquid phase to the gaseous one. The VOO adulteration by ROO causes a slightly increasing density (figure 2.G). Effectively, olive oil refining allows addition of some chemical compounds like anti-oxidants and stabilizing species that can increase VOO density. This can also be explained primarily by the concentration of polyphenols and then know the number of oxidation of the oil to be analyzed [29].

Conclusion

The virgin olive oil produced in the two Moroccan geographic sites, Demnat and Tagzirt, presents some chemical and physical characteristics like free acidity, peroxide content that are consistent with those recommended by the international olive oil council (IOOC) standards. However, other characteristics like water content and density would be outside of these standards. Sunlight promotes the acidity of virgin olive oil and its oxidation. Temperature makes increasing virgin olive oil free acidity and peroxide content. Demnat and Tagzirt virgin olive oils present a considerable decreasing of peroxide index when they are adulterated by refined olive oil. Acid index values of Tagzirt virgin olive oil are higher than those of Demnat virgin olive oil. Acid index of the two virgin olive oils decreases, after adding refined olive oil, especially below 10% of ROO. Globally, virgin olive oil from Demnat would present characteristics that allow it a better performance resistance to temperature, sunlight and adulteration. Further studies are necessary in order to confirm such discrimination in terms of resistance.

As perspective of this work we will compare these results concerning the "Moroccan Picholine" variety to those on other olive varieties. In particular, "Haouzia" and "Manera" varieties from Morocco, "Picholine du Languedoc" from France and "Arbequina" and "Picual" from Spain.

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References

1. Fernandez-Orozco R., Roca M., Gandul-Rojas B., Gallardo-Guerrero L. *Journal of Food Composition and Analysis*. 24 (2011) 858.
2. Bouzid O., Navarro D., Roche M., Asther M., Haon M., Delattre M., Lorquin J., Labat M., Asther M., Lesage-Meessen L. *Process Biochemistry*. 40(2005) 1855.
3. Landete J.M., Curiel J.A., Rodríguez H., De las Rivas B., Muñoz R. *Food Chemistry*. 107 (2008) 320.
4. Lerma-García M.J., Herrero-Martínez J.M., Ramis-Ramos G., Simó-Alfonso E.F. *Food Chemistry*. 108 (2008) 1142.
5. Oueslati I., Anniva C., Daoud D., Tsimidou M.Z., Zarrouk M. *Food Chemistry*. 112 (2009) 733.
6. Roca M., Mínguez-Mosquera M.I. *Journal of Plant Physiology*. 160 (2003) 451.
7. Koprivnjak O., Moret S., Populin T., Lagazio C., Conte L.S. *Food Chemistry*. 90 (2005) 603.
8. Alcántara E., Cordeiro A.M., Barranco D. *Journal of Plant Physiology*. 160 (2003) 1467.
9. Montaña A., Sánchez A.H., Casado F.J., De Castro A., Rejano L. *Food Chemistry*. 82 (2003) 297.
10. Direction de l'Enseignement, de la Recherche et du Développement. Ministère d'Agriculture, du Développement Rural et des Pêches Maritimes. Royaume du Maroc. Bulletin mensuel d'information et de liaison du PTTA. 141 (2006) 3
11. Kalogeropoulos N., Kaliora C.A., Artemiou A., Giogios I., *LWT - Food Science and Technology*, In Press, Corrected Proof, Available online 28 February 2014
12. Guillén M.D., Uriate P.S. *Food Chemistry*. 134 (2012) 162.
13. Pristouri G., Badeka A., Kontominas MG. *Food Control*. 4 (2010) 412.
14. Kim M., Lee S., Chang K., Chung H., Jung Y.M. *Analytica Chimica Acta*. 748 (2012) 58.
15. Elbir M., Moubarik A., Rakib E.M., Grimi N., Amhoud A., Miguel G., Hanine H., Artaud J., Vanloot P. and Mbarki M. *Maderas ciencia y tecnología* 14 (2012) 361.
16. Codex Stan 33. 1981.
17. Orlandi F., Bonofiglio T., Romano B., Fornaciari M. *Scientia Horticulturae*. 138 (2012) 151.
18. Herrero A.M., Carmona P., Pintado T., Jiménez-Colmenero F., Ruíz-Capillas C. *Food Research International*, Volume 44 (1) (2011) 360
19. Ciafardini G., Zullo B.A. *Food Microbiology*. 19 (2002) 105.
20. Lavermicocca P., Francesco Russo M.R., Srirajaskanthan R. *Olives and Olive Oil in Health and Disease Prevention*. (2010) 735
21. Tassou C.C., Panagou E.Z., Nychas G.J.E. *Olives and Olive Oil in Health and Disease Prevention*. (2010) 397
22. Owen R.W., Giacosa A., Hull W.E., Haubner R., Spiegelhalder B., Bartsch H. *European Journal of Cancer*. 36 (2000) 1235.
23. Nakbi A., Issaoui M., Dabbou S., Koubaa N., Echbili A., Hammami M., Attia N. *Journal of Food Comp. and Analysis*. 23(2010) 711.

24. Simões P.C., Carmelo P.J., Pereira P.J., Lopes J.A., Da Ponte M.N., Brunne G. *The Journal of Supercritical Fluids*. 13 (1–3) (1998) 337
25. Simões P.C. and Brunner G. *The Journal of Supercritical Fluids*. 9(2) (1996) 75
26. Valdés A.F., Garcia A.B. *Food Chemistry*. 98(2006) 214.
27. Nissiotis M., M. Tasioula-Margari M. *Food Chemistry*. 77(2002) 371.
28. Kalogianni E.P., Karapantsios T.D., Miller R. *Journal of Food Engineering*. 105(2011) 169.
29. Larif M., Ouhssine M., Soulaymani A. and Elmidaoui A. *Research on chemical intermediate*. DOI: 10.1007/s11164-013-1267-0 (2013)

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