Volatile constituents and oxidative stability of virgin olive oils: influence of the kneading of olive-paste

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1. INTRODUCTION

Virgin olive oils extracted with gentle physical procedures show unique organoleptic and nutritional properties as compared to those of other vegetable oils. The extraordinary aroma of virgin olive oils is influenced by several production and processing parameters (Montedoro et al., 1986), such as the agronomic choices, olive cultivar, ripening degree and sanitary quality of olives, harvest system, post-harvest storage of fruits, processing technology and oil bottling and storage. Among these parameters, processing technology seems to greatly determine the final quality of the oil. It is well known that the organoleptic properties of virgin olive oils are significantly affected by the crushing method, the kneading process of the olive-paste, and the separation systems of crude oil or oil-water mixture from the olive-paste. All researchers and processing plant operators have underlined the negative effect of high temperatures and long processing time on the organoleptic quality of the oil (Montedoro et al., 1994).

On the other hand, the mechanisms of formation of some volatile constituents of olive oil aroma have recently been reported (Olias et al., 1993; Di Giovacchino et al., 1996). The biochemical lipoperoxidation generated 13-hydroperoxides from linoleic and linolenic acids, which decompose into a series of aliphatic C-6 volatile compounds following other enzymic patterns. These volatile compounds are actually secondary products, i.e. they are formed as a result of disruption of cell structure.

In the present work, the interaction between olive-paste kneading, oxidative stability and aroma constituents of virgin olive oils is investigated.

2. EXPERIMENTAL

Five Kg of olives from Frantoio and Moraiolo cultivars were ground together by a metal crusher...

The accelerated oxidation rates were plotted with a fatty substances (NGD C-10, 1976; NGD C-35, 1976). The accelerated oxidation rates were plotted with a Rancimat mod. 679 (Metrohm AG, Herisau, Switzerland) at 110°C; the rate of air flow through the samples was set to 20 L/h; the volatile reaction products were caught into measured vessels containing 60 mL of distilled water.

Volatile components were determined after collection by a charcoal cartridge absorption and directly injection into capillary gas chromatograph apparatus equipped with a MW-1 Microwave Sampler (J. Rektorik, Geneva, Switzerland) as injector, and a capillary polar column 30 m x 0.3 mm i.d., 1 µm of film thickness (Restek Stabilax, Stepbio, Bologna, Italy) (Bocci et al., 1992; 1994).

For the minor polar components (MPCs) extraction, 10 g of each oil were homogenized with 10 mL of a methanol/water mixture (80:20, v/v) for 1 min, using an Ultra-Turrax (Janke & Kunkel, Ika Labortechnik, Staufen, Germany) at the lowest homogenization speed. After centrifugation, the methanol solution was separated and the extraction was repeated twice. The three methanol extracts were combined and vigorously washed with 50 mL of n-hexane. This mixture was again centrifuged and then the hydro-alcoholic layer was evaporated to dryness with a rotary evaporator at 50°C, using anhydrous methanol for water elimination. The residue was redissolved in 10 mL of methanol and the solution obtained was divided into two like portions. The first one was transferred into the reaction vessel of Rancimat and evaporated to dryness with nitrogen flow, whereas the second one was analyzed by reversed phase-HPLC (RP-HPLC) and capillary gas chromatography (CGC) after silanization (Sweeney et al., 1963).

RP-HPLC analysis was carried out by a Varian Star 9010 (Valhnut Creek, CA) equipped with a Spherex 3 ODS column (150 x 4.6 mm) (Phenomenex, Torrance, CA) and a Polychrom 9065 diode-array detector set at 278 nm. The solvent elution program is reported in Table I.

CGC analysis of trimethylsilyl ethers (TMS) of MPCs extracted from the oils was carried out with a Carlo Erba (Milano, Italy) HRGC mod. Mega 5160 equipped with a flame ionization detector (FID) and a fused silica capillary column (25 m x 0.32 mm i.d.) coated with SE 52 (0.1-0.15 µm film thickness) (Supelco, Bellefonte, CA). Oven temperature was kept at 50°C for 1 min, then programmed from 50°C to 300°C at 3°C/min and maintained at this final temperature for 10 min.

### Table I

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Acetic Acid (% in water)</th>
<th>Methanol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>18</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>28</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

### Table II

Volatile aldehides content at different kneading times

<table>
<thead>
<tr>
<th>Kneading Time (min)</th>
<th>Hexanal (% of total constituents)</th>
<th>trans-2-hexenal (% of total volatile constituents)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4,0</td>
<td>19,3</td>
</tr>
<tr>
<td>20</td>
<td>4,8</td>
<td>46,7</td>
</tr>
<tr>
<td>40</td>
<td>5,8</td>
<td>51,6</td>
</tr>
<tr>
<td>70</td>
<td>7,1</td>
<td>45,2</td>
</tr>
</tbody>
</table>
At the end of kneading, the contact between the oil and the olive-paste is interrupted. From this point onwards, the amount of trans-2-hexenal present in the oily-phase slowly diminishes due to both a diffusion and a redox mechanisms. Under these conditions, chemical oxidation reactions are responsible of any changes of composition as progressive decrease of trans-2-hexenal and increase of hexanal. This hexanal rise can drastically modify the organoleptic profile of the oil which, in extreme deterioration conditions, can present a rancidity odor.

Conventional olive processing plants usually produce oils having a normal or a particularly intense olive oil odor, except for those situations in which one or more processing parameters are greatly modified. In this case, the resulting shelf life of the virgin olive oil is directly conditioned by these processing variations.

Rancimat stability test of the oils extracted from the olive-paste at different kneading times evidence a progressive reduced «induction period» (Figure 2). Peroxide value, (PV) not significantly vary (Table III) during kneading, probably due to the peroxide oxidative action against other oil components, such as MFCs with antioxidant activity (i.e. polyphenols). This assumption agrees, in fact, with the RP-HPLC (Montedoro et al., 1993; Angerosa and Di Giacinto, 1995; Evangelisti et al., 1997) (Figure 3) and CGC (Figure 4) profiles of the MFCs extracted from the virgin olive oils obtained by centrifugation of the olive-paste/oil during the kneading test.

Figure 5 shows the Rancimat traces of a refined seed oil added with the MFCs extracted from the virgin olive oils obtained from the kneading test. These results reflect a reduction of the natural antioxidant contents during kneading, due to enzymic peroxidation. In fact, the Rancimat time is related to the kneading time of olive-paste.
Considering all these facts, the choice of the processing plant and the technological parameters for virgin olive oil production must take into account that the olive-paste/oil contact is a determinant factor for the characteristics of the final product.

The results reported in this study evidence that, in order to compare different processing plants, a previous «normalization» of at least one parameter of the virgin olive oil, such as the qualitative and quantitative polyphenol contents or the aroma characteristics, would be necessary. Up to now, the different technologies from the several commercial plants have, in fact, been misinterpreted because the tests have been performed without knowing how the single experimental conditions could affect the final quality of the oil.

**BIBLIOGRAPHY**


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