"Veiled" Extra-Virgin Olive Oils: Dispersion Response Related to Oil Quality

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A cloudy ("veiled") extra-virgin olive oil was stored 10 mon at room temperature and monitored at 15-d intervals. The oil was very stable under oxidizing conditions; a slight increase in free acidity (from 0.2 to 0.3%, expressed as oleic acid), a notable rise in the amount of diacylglycerols and a minor increase in peroxide content were observed. Turbidity disappeared after a few months due to chemical bonding between a nitrogen-containing component and the free acids that were released over time. The material in suspension, therefore, contained some chemical groups capable of acting as antioxidants.

KEY WORDS: Cloudy oil stability, extra-virgin olive oil, natural antioxidant, natural buffer.

Extra-virgin olive oils are characterized by a post-pressing emulsion or dispersion which is a metastable blend of phases. This condition can persist for several months before turning into a separate-phase system (deposit), i.e., a brown-colored residue that settles to the bottom of the container and is usually unacceptable to consumers. However, there has recently been a market resurgence of "veiled" extra-virgin olive oils that meet consumer preference because of the "green," nonoverprocessed appearance of the oils. The characteristics of the dispersion–suspension phenomenon exhibited by virgin oils vary with the extraction system used, resulting in different appearances and settling times. Although dispersion traditionally has been considered a positive phenomenon in virgin oil, it has not yet been mentioned in the literature. The objective of this study was to investigate the effects of dispersion on extra-virgin olive oils in relation to their shelf life.

EXPERIMENTAL PROCEDURES

Materials. The analytical-grade solvents and reagents were supplied by Carlo Erba (Milan, Italy). All extra-virgin olive oils were made from the same batch of olives by different extraction systems: traditional (milling followed by hydraulic pressing), Baglioni (milling followed by pressing through alternating layers of olive stones and paste), or continuous or "Sinolea" (filtration with decantation). The Sinolea oil was stored for 10 mon at room temperature and monitored at 15-d intervals.

Methods. Free acidity and peroxide value were determined according to the *Official Methods of Analysis* for fatty substances (1). The accelerated oxidation rates were plotted with a Metrohm Rancimat at 110°C and 20 L/h air flow. Free fatty acids and diacylglycerols (diglycerides) were simultaneously determined, as suggested by Frega *et al.* (2), in a polar-column gas chromatograph (TAP; Chrompack, Middelburg, The Netherlands).

The deposit residue from extra-virgin olive oil after 10 months' storage was treated with a diethyl ether solution of diazomethane prepared by the method of Fieser and Fieser (3). Transmethylation of the deposit residue was carried out with 5% hydrochloric acid in methanol (4).

RESULTS AND DISCUSSION

To get a valid comparison of the oxidative stability of lipid systems as determined by Rancimat, only one of their parameters was changed at a time, i.e., processing technique (or one step of it) while using the same olive batch. Although it is still not possible to convert the Rancimat values into real shelf-life terms, it is known that high induction times correspond to long shelf lives. Figure 1 shows the Rancimat curves of the traditional and Baglioni extra-virgin olive oils. The induction time of the Baglioni oil (Fig. 1, oil 2) was 8% higher than that of the traditional type (Fig. 1, oil 1), meaning that the Baglioni oil may have a longer shelf life than the traditional one.

Samples of the same oils were then filtered to eliminate the "veiling" (Fig. 1, 1* and 2*). Samples of filtered and nonfiltered oils were incubated for 14 h at 40°C (samples in square brackets) and subjected to Racimat testing. The induction times (Fig. 1) of the filtered and incubated samples were lower than those of the untreated oils, whereas the induction times were even smaller for the samples subjected to both treatments. This suggests that the material in dispersion (about 8% of the oil composition) exerts a positive stabilizing effect on the oil. These facts also eliminate the hypothesis that this material was rich in water and enzymes of plant origin because an increase in the degree of oxidation would have been observed in its presence, especially in the incubated samples.

On the other hand, the stability of a fatty substance is also affected by progressive acidification, due to hydrolysis of the acylglycerides' components, which induces a

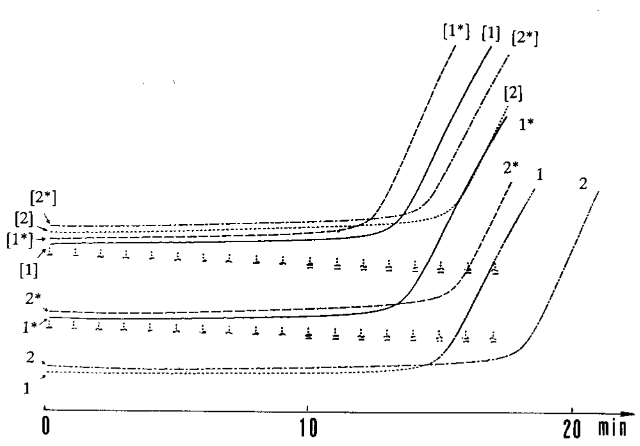

FIG. 1. Rancimat curves of the extra-virgin olive oils. 1, traditional oil; 2, Baglioni oil; 1*, oil 1 after filtration; 2*, oil 2 after filtration; [1], oil 1 after incubation for 14 h at 40°C; [1*], oil 1* after incubation; [2], oil 2 after incubation; [2*], oil 2* after incubation.

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taste degradation. Although this degradation is less important than that caused by oxidation, a rise in acidity could make an oil lose its commercial ranking (especially in the EEC countries), with consequentially economic drawbacks or even legal complications. To establish to what extent oil acidity may be influenced by the emulsion, a given amount of Sinolea oil was stored for 10 mon. Samples were taken at 15-d intervals and placed in a freezer at −20°C. During storage, a small increase in acidity (from 0.2 to 0.3%) was observed, even though the acylglyceride composition registered an increase in the amount of 1,3-diacylglycerols, indicating lipolysis (2). Nevertheless, further gas-chromatographic analysis (Fig. 2) (2) showed no significant rise in free acids. To clarify this apparent contradiction, the residue on the bottom of the container was separated and titrated, giving an acidity of 0.6%. This indicates that the free acids, produced by lipolysis, bonded the residue and precipitated with it.

This assumption was further tested by washing the deposited residue several times with hexane. A sample of this extract was then treated with a diazomethane/diethyl ether solution. The gas-chromatographic analysis of the diethyl ether phase showed that fatty acid methyl esters were not formed under these conditions. Another sample of the washed residue was then treated with transmethylation reagents for 1 h at 105°C. In this case, gas-chromatographic analysis of the extract registered high amounts of methyl esters. These results show that the free acids are chemically bound to the particles of the dispersed material, which acts as a buffer against the normal rise of acidity during storage. This effect is likely to be related to the precipitation of the dispersed particles because the partial change in the surface charges would bring about a subsequent coagulation of the colliding particles with opposite charges.

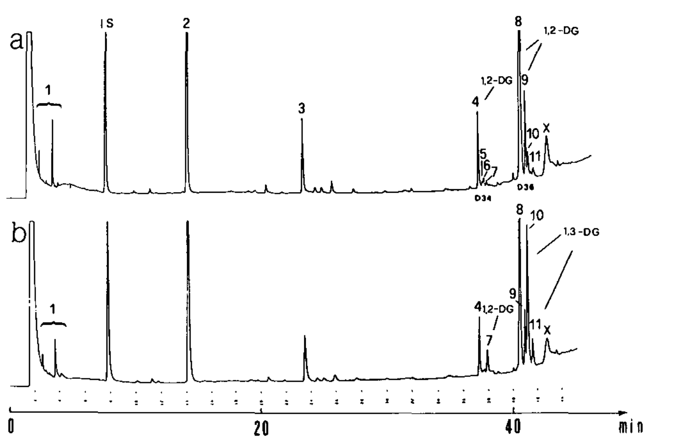

FIG. 2. Gas chromatographic traces of polar components of the Sinolea oil stored at room temperature for (a) O and (b) 315 d. 1, Free fatty acid methyl esters; IS (internal standard), squalane; 2, squalene; 3, α-tocopherol; 1,2-DG, 1,2-diacylglycerol; 1,3-DG, 1,3-diacylglycerol; 4, palmityl-oleine; 5, palmitoyl-oleine; 6, palmityl-linoleine; 7, 1,3-palmityl-oleine; 8, 1,2-oleyl-oleine; 9, 1,2-oleyl-linoleine; 10, 1,3-oleyl-oleine; 11, 1,3-oleyl-linoleine; X, unidentified components.

Regarding the composition of the deposited residue, a nonnegligible amount of nitrogen was found (0.6% in a wet basis), most probably in the form of protein substances. After transmethylation (heat treatment in acid methanol) of the deposit residue, a certain rise in small-sized polyphenol components was also observed. These components, formed by hot acid hydrolysis, indicate the polyphenolic (perhaps polymeric) nature of this material. The suspended and dispersed particles that constitute the "veiling" of extra-virgin olive oils play a stabilizing role in the oil's shelf life, acting as antioxidants and as a buffer in the system against increasing acidity. These effects are so positive that avoidance of oil filtration should be advised as means of extending the oil's shelf life and enhancing its quality. In fact, quality improvements in a year-old or low-quality oil can be induced by re-treating them with the Baglioni system, which regenerates the dispersion. The material in suspension–dispersion that "veils" extra-virgin olive oils is, therefore, an ideal food additive because it acts as an acidity buffer and antioxidant without affecting the taste qualities of the oil, and it does not produce soluble derivatives that somehow may be problematical for the consumer.

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