

# The phenolic profile of virgin olive oil is influenced by malaxation conditions and determines the oxidative stability

**Authors:** H. Miho, J. Moral, M. A. López-González, C.M. Díez\*, F. Priego-Capote\*  
 University of Cordoba. Faculty of Agronomy. Department of Agronomy. E-mail: hmiho@uco.es



## Abstract

Phenolic compounds largely contribute to the nutraceutical properties of virgin olive oil (VOO), to the organoleptic attributes and to the shelf life due to their antioxidant capabilities. Considering the relevance of malaxation in the oil extraction process, we tested the effects of malaxation time on the concentrations of relevant phenolic compounds in VOO, and we evaluated the influence of performing malaxation under vacuum conditions. An increase in malaxation time significantly decreased the concentrations of aglycon isomers of oleuropein and ligstroside but, conversely, increased the oleocanthal and oleacein contents. Additionally, malaxation under vacuum led to an increase in phenolic contents compared to standard conditions carried out at atmospheric pressure. Finally, we explored the possibility of predicting the VOO oxidative stability on the basis of the phenolic profile, and a model ( $R^2 = 0.923$ ;  $p < 0.0001$ ) was obtained by combining the concentration of the VOO phenolic compounds and the main fatty acids.

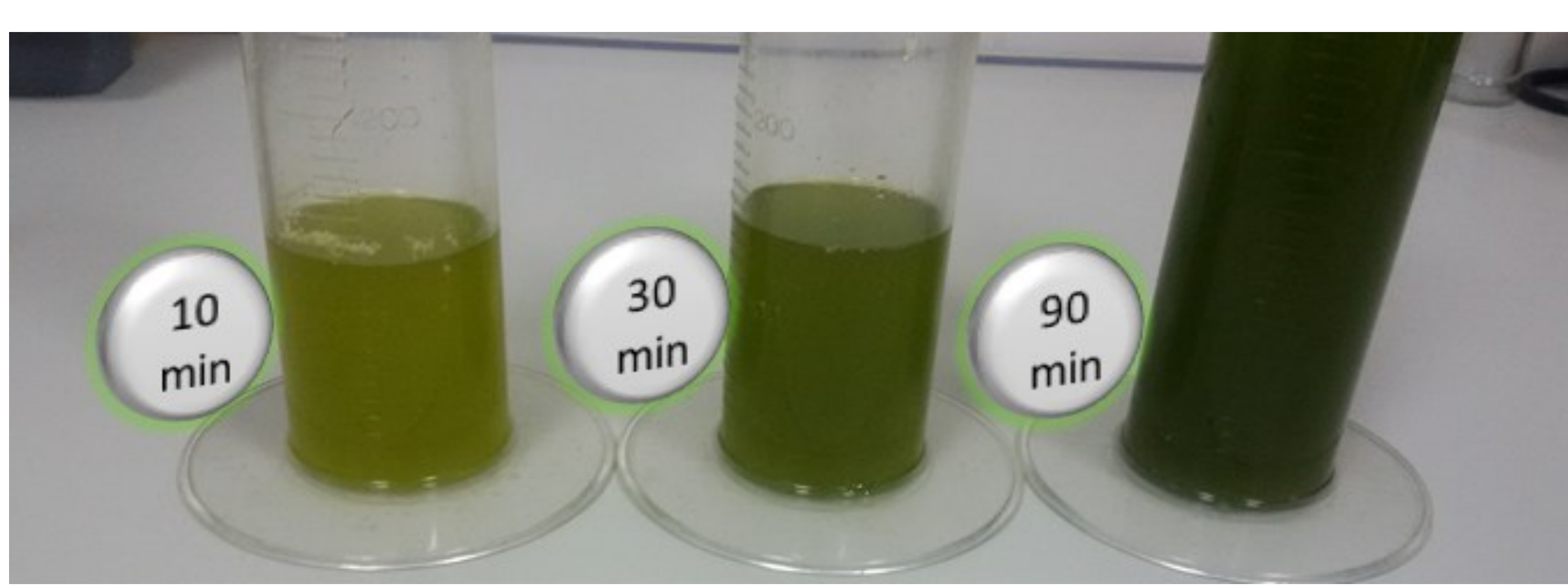
## Material and methods

Olive fruit samples were collected during the 2017/2018 crop season from an experimental orchard located at the World Olive Germplasm Bank of Cordoba University. Three experiments were designed to accomplish the proposed goals of this study: the first and second experiments were aimed at evaluating the influence of malaxation time (6 cultivars  $\times$  3 MTs  $\times$  3 replicates = 54 samples) and malaxation under vacuum conditions (6 cultivars  $\times$  2 extraction conditions  $\times$  3 replicates = 36 samples) on the phenolic profile. The third experiment evaluated the association of the VOO oxidative stability to its phenolic and fatty acid composition (900 VOO samples). Six different cultivars ('Arbosana', 'Bosana', 'Blanqueta', 'Coratina', 'Frantoio' and 'Mixani') showing remarkable diversity in their phenolic profiles according to Miho et al. (2018) were selected for the study. Determination of the fatty acid composition of VOO samples was carried out by GC-FID analysis after derivatization by transesterification. Phenolic analyses were performed by reversed-phase liquid chromatography followed by electrospray ionization (ESI) in negative mode and tandem mass spectrometry (MS/MS) detection. The oxidation stability index was measured by the Rancimat Method using a 743 Rancimat System from Metrohm.

## Results

### EFFECT OF MALAXATION TIME ON THE PHENOLIC COMPOSITION OF OLIVE OILS:

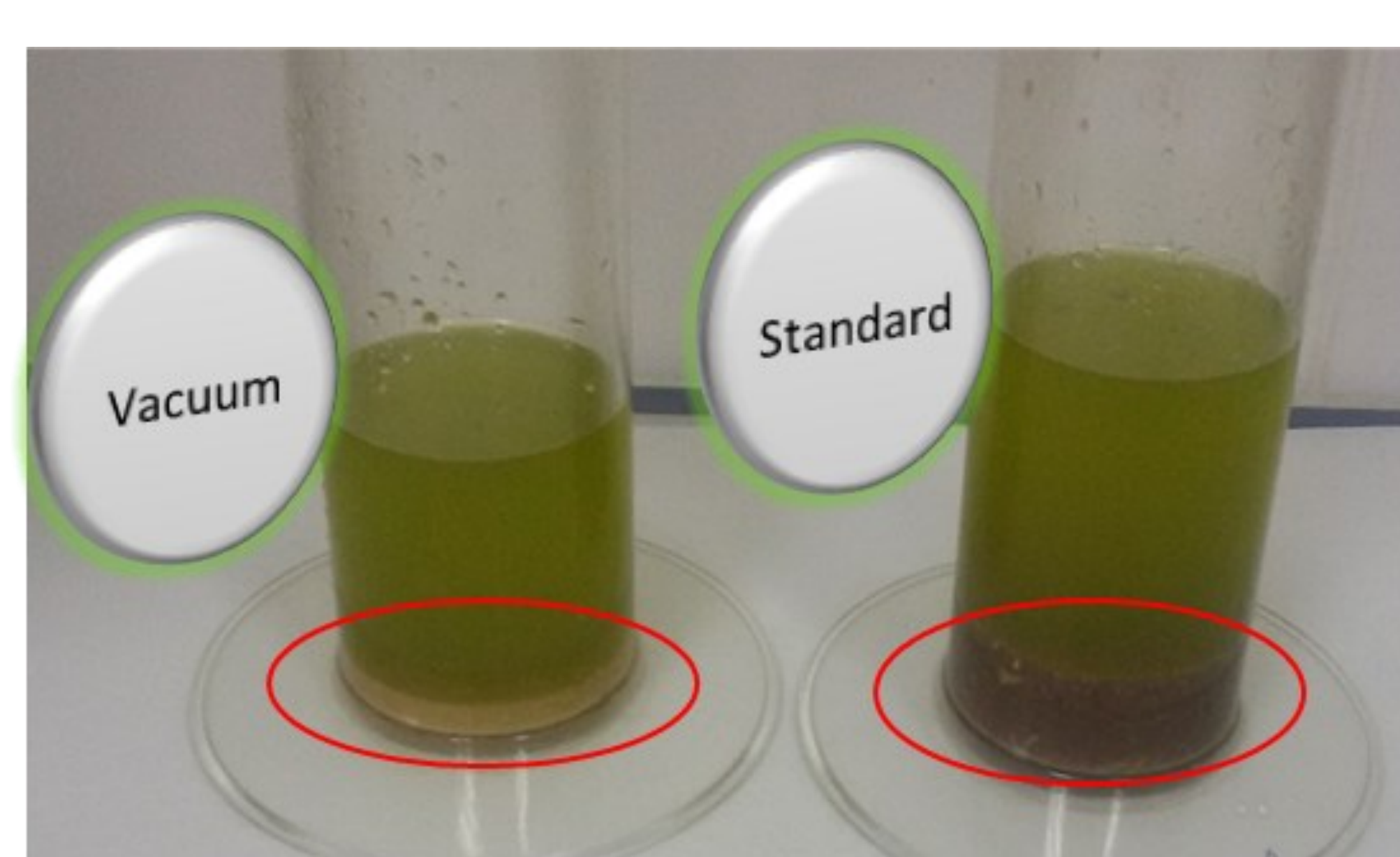
The increase in the malaxation time generally reduces the phenolic concentration in the olive oil. But on the contrary, oleocanthal and oleacein increase their concentration. Nevertheless, the magnitude of this last effect also depends on the genetic factor and not all cultivars behave in the same way.



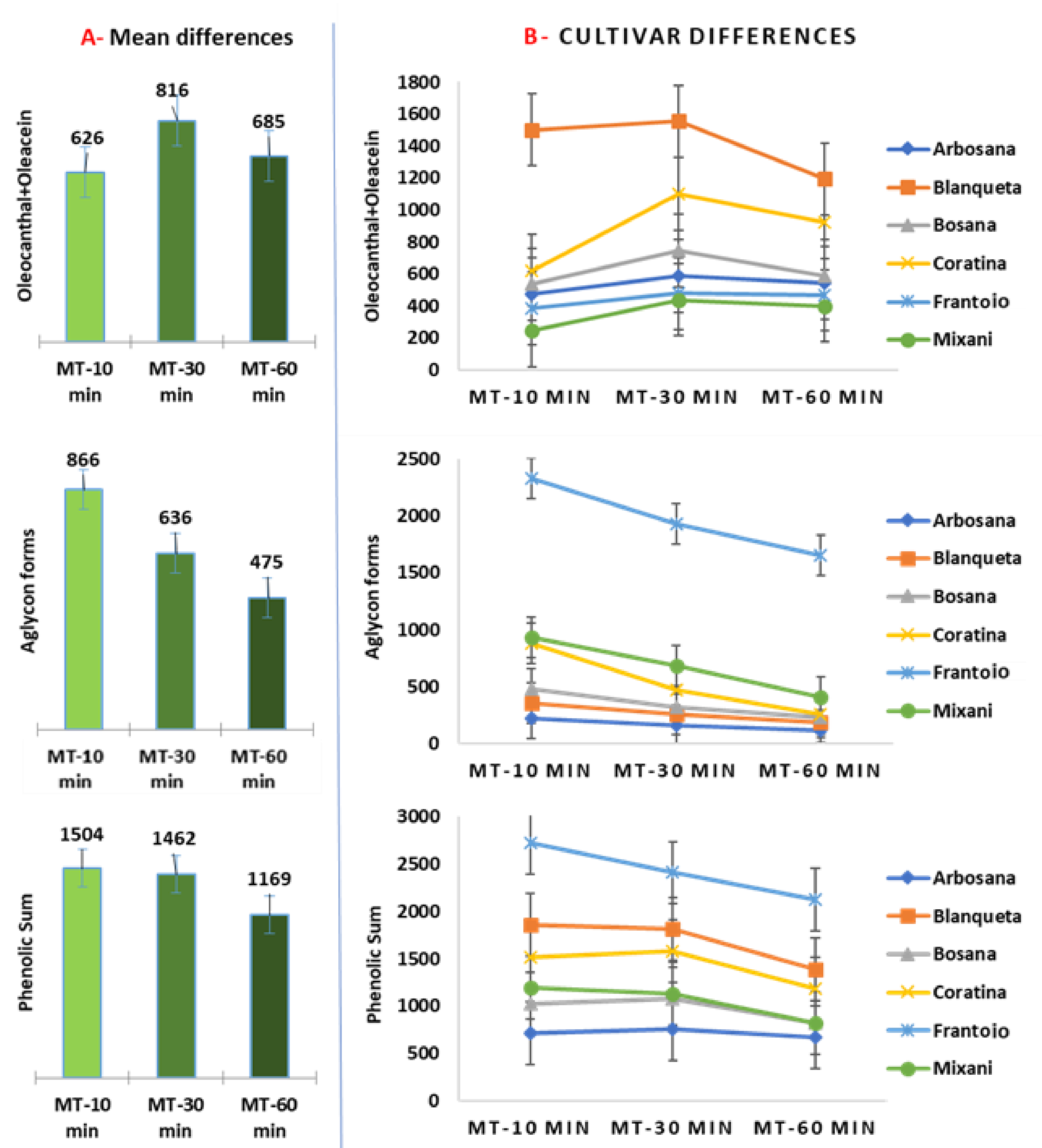
The colour variation of the olive oil during the malaxation time

### EFFECT OF EXTRACTION UNDER VACUUM CONDITIONS ON THE PHENOLIC COMPOSITION OF OLIVE OILS:

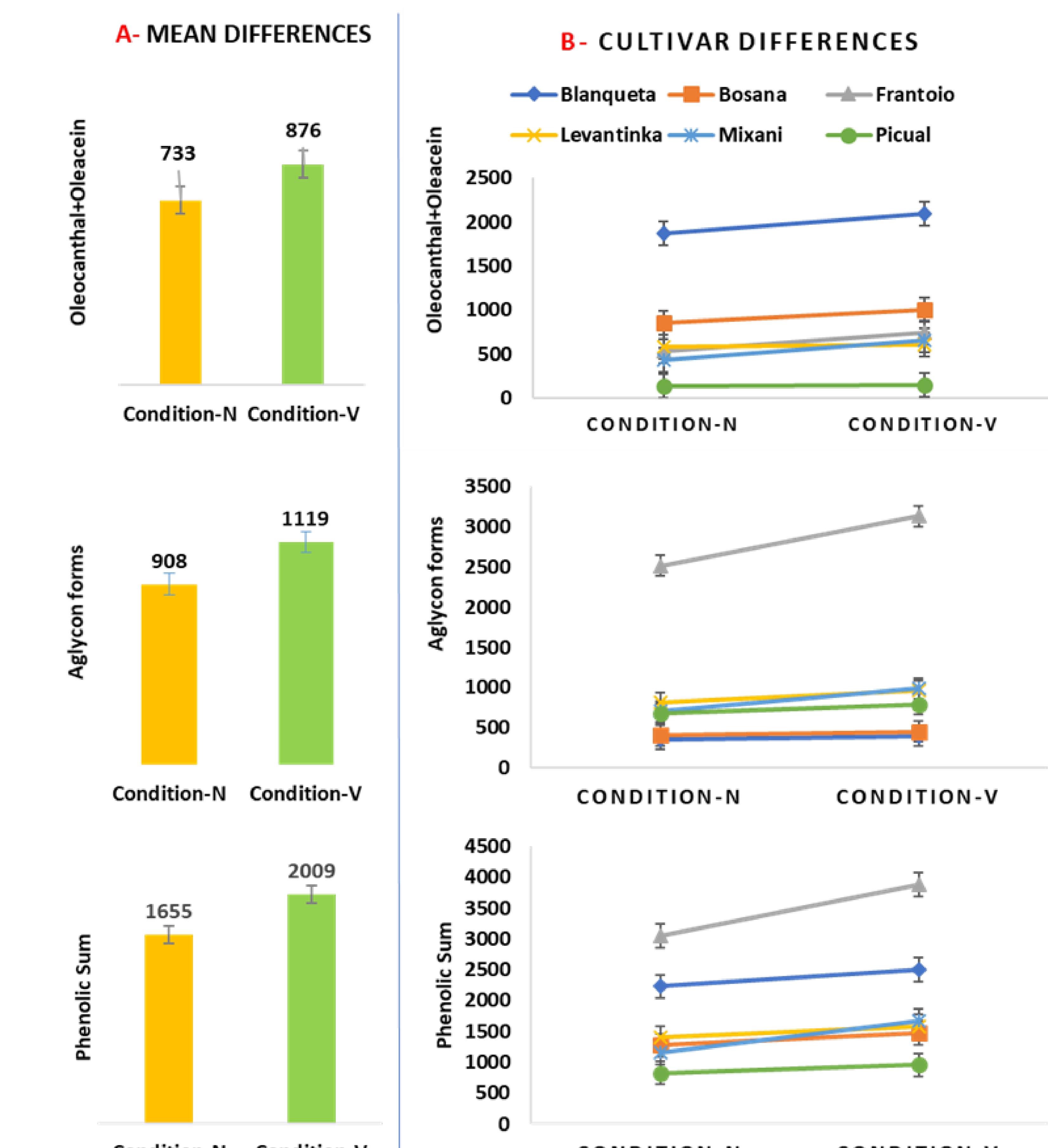
The implementation of the vacuum conditions during the malaxation process significantly increases the total phenolic content by at least 20% as compared to standard conditions.



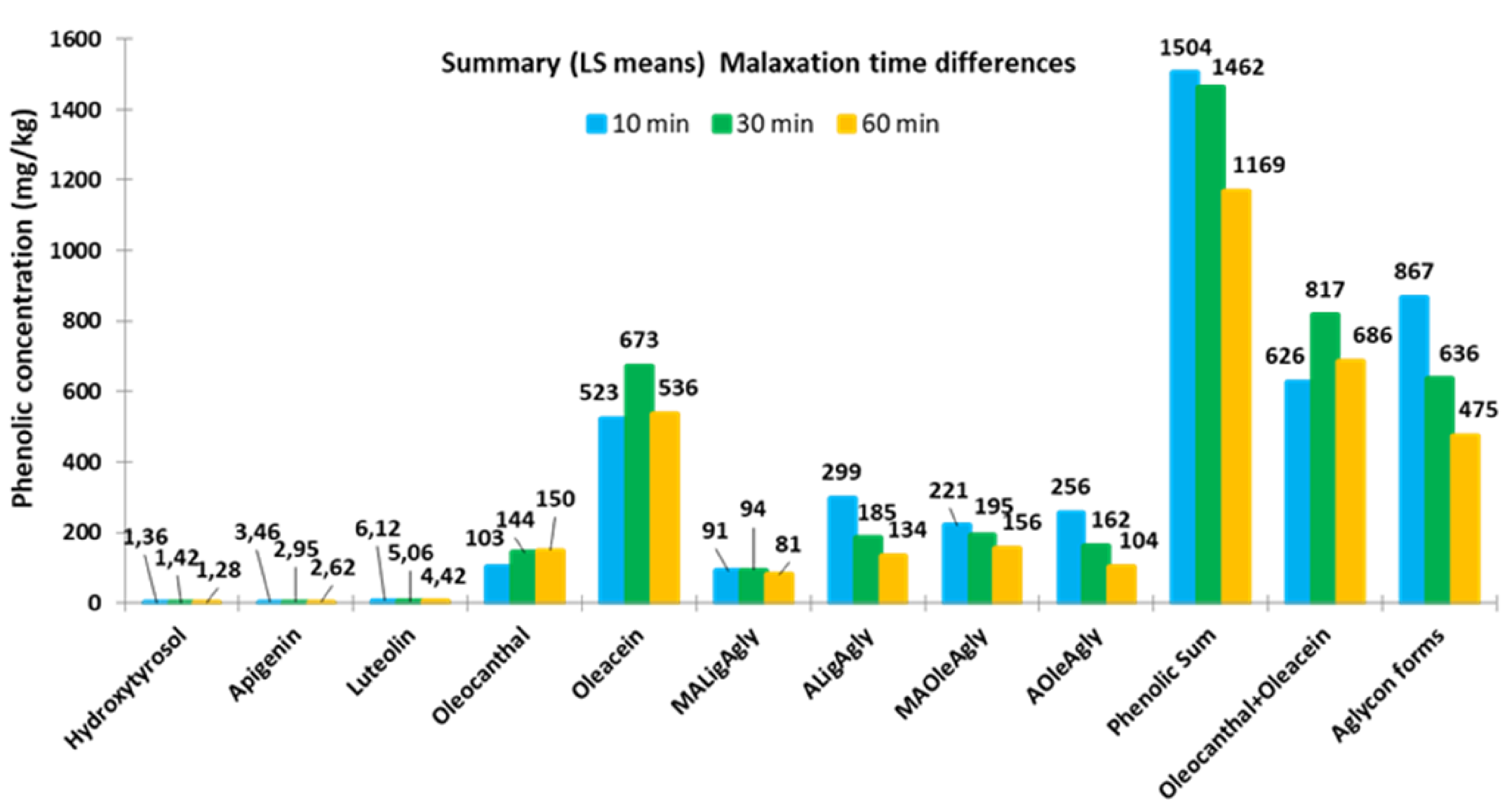
Colour differences between oils obtained under vacuum and standard conditions



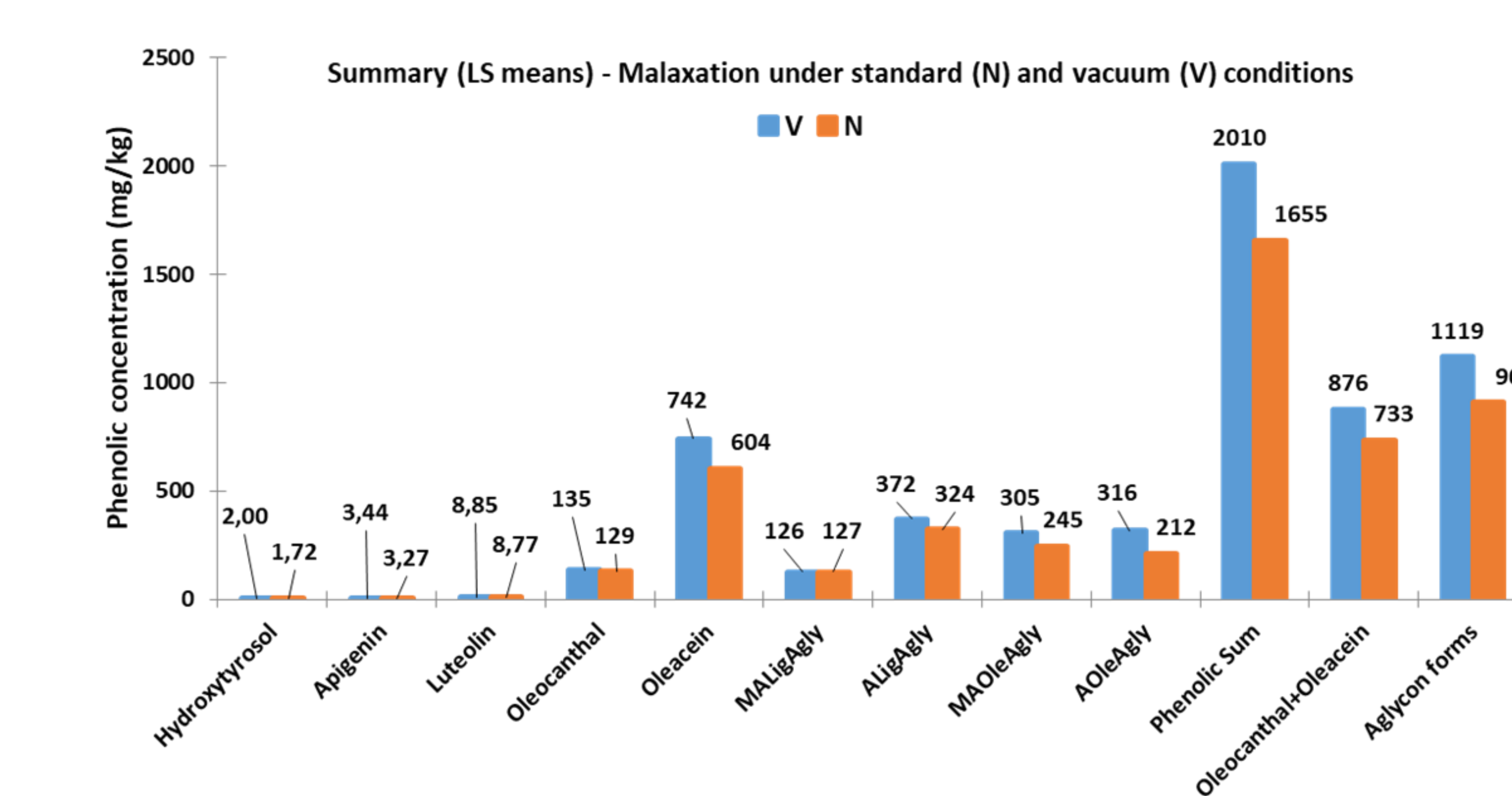
(A) Mean differences for the main groups of phenolic compounds found in olive oil from six cultivars processed at three different malaxation times. (B) Phenolic concentrations for each cultivar processed at three different malaxation times. Phenolic concentrations are expressed in mg/kg.



A- Mean differences for the main groups of phenolic compounds found in olive oil from six cultivars processed at two different malaxation conditions: under vacuum or standard conditions. B- Phenolic concentrations for each cultivar processed at two different malaxation conditions. Phenolic concentrations are expressed in mg/kg. (N – standard or atmospheric condition; V – vacuum condition).



Mean concentration of phenolic compounds in VOO from six cultivars at three malaxation times.

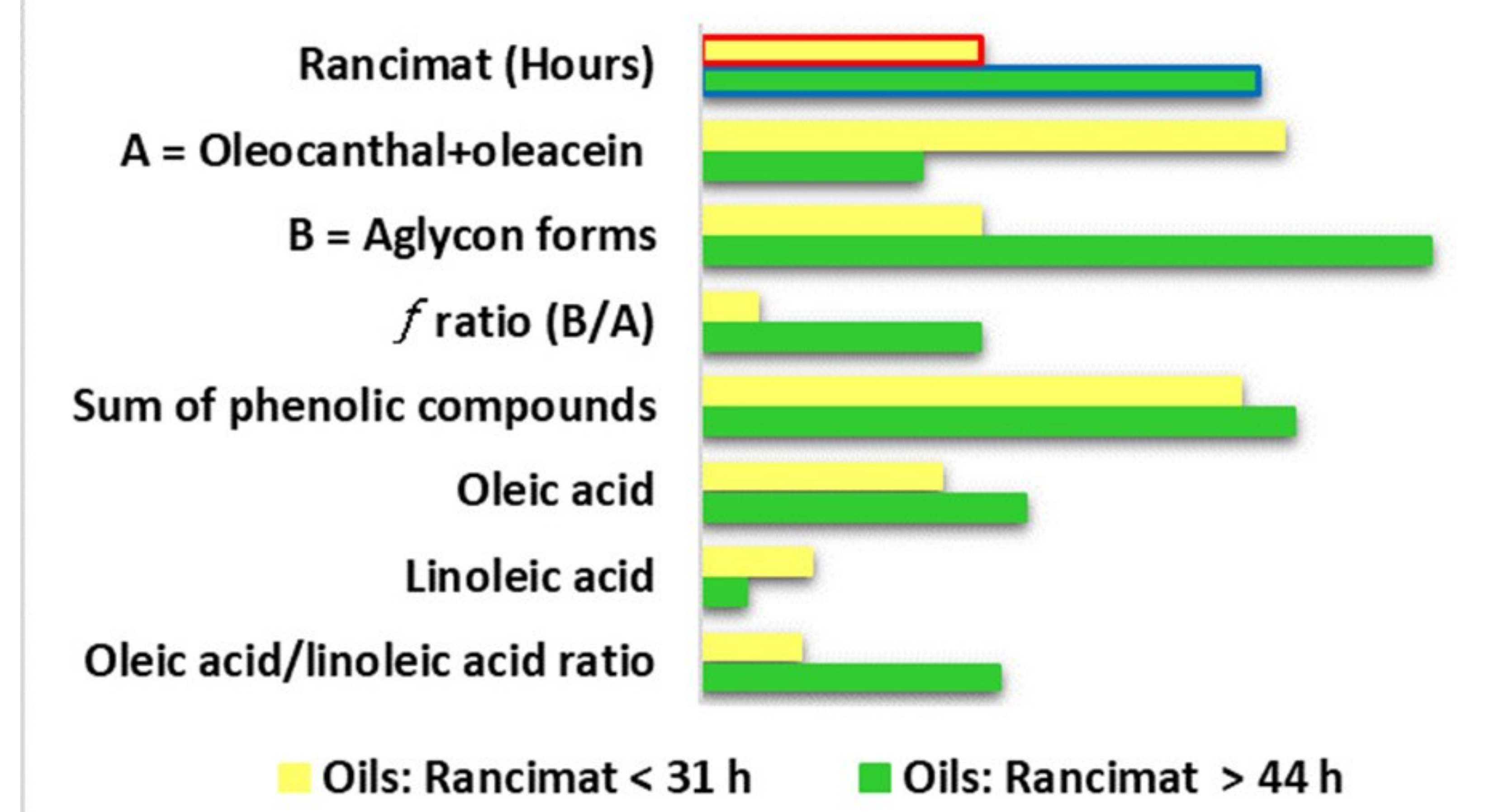


Mean concentration of phenolic compounds in VOO from six cultivars obtained by applying vacuum during malaxation or under atmospheric pressure.

## Role of phenols in the VOO Oxidative Stability (OS) and development of an OS predictive model

The oxidative stability of olive oil is mainly defined by its fatty acid and phenolic composition. Oils richer in aldehydic forms of oleuropein and ligstroside aglycone, and richer in oleic acid, tend to be much more stable than oils of other profiles. Likewise, knowing the phenolic and fatty acid composition, the oxidative stability of the VOO could be estimated throughout mathematical models.

### Phenolic ratio or "f" ratio

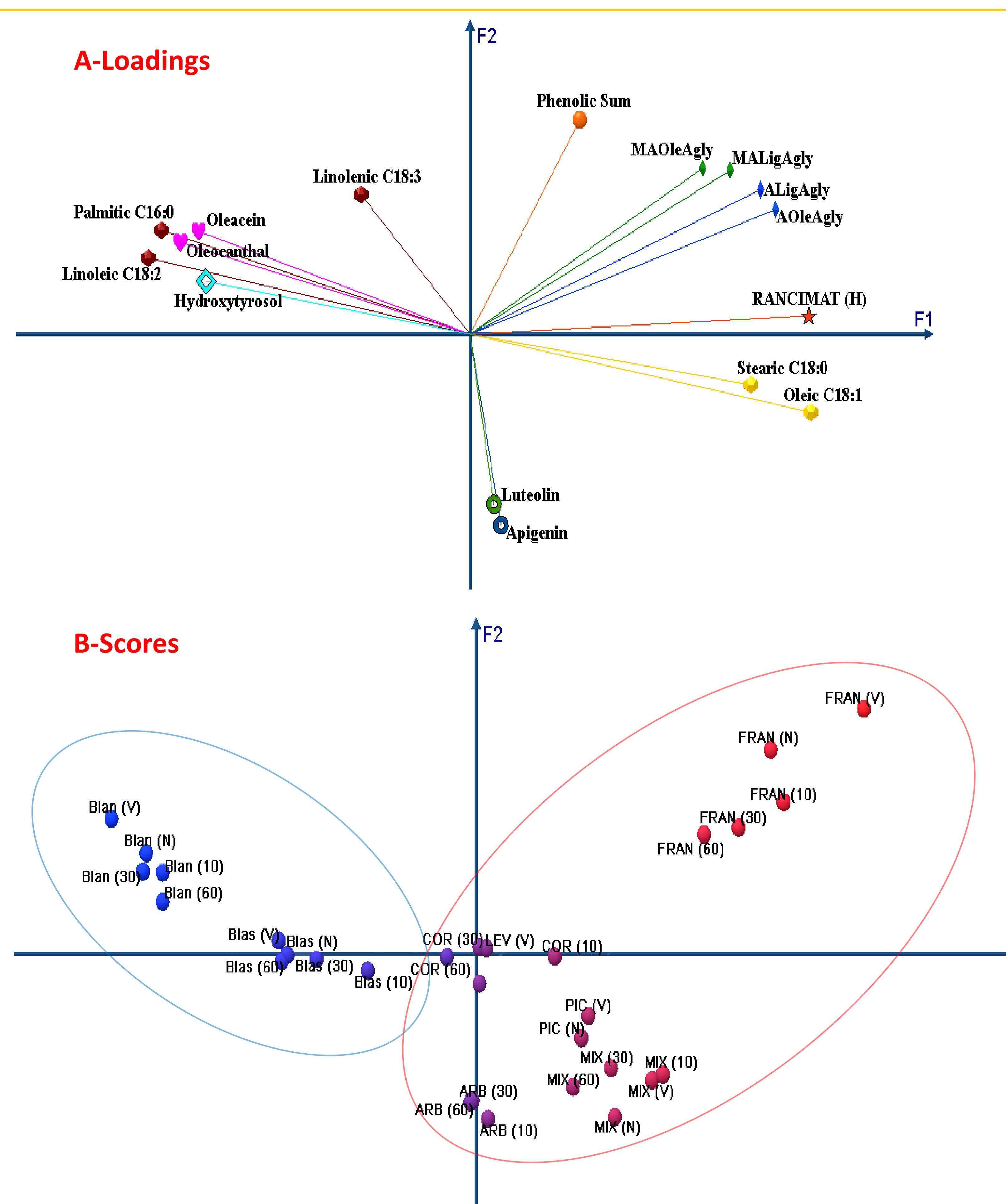


Cultivar	Mean St* (h)
Picual	58,63
Frantoio	58,53
Mixani	45,65
Coratina	44,64
Arbosana	42,09
Levantinka	30,52
Blanqueta	25,31
Bosana	23,93

\*Stability (RANCIMAT)

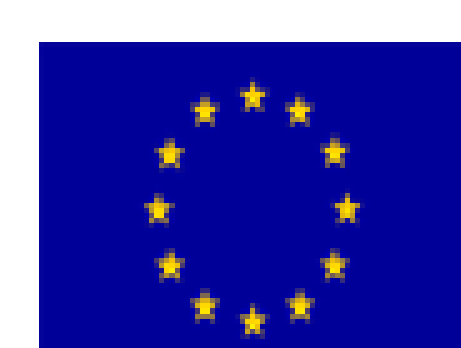
Mathematic model to estimate the Oxidative Stability (OS) expressed as Rancimat hours:

$$OS \text{ (Hours)} = (49.603) + (5.348 \cdot \text{hydroxytyrosol}) + (0.029 \cdot \text{AOleAgly}) + (-1.625 \cdot \text{Linoleic acid})$$



The loading plot (A) and scores plot (B) of the principal component analysis of olive oil samples obtained from eight cultivars. PCA was done using the concentrations of phenolic compounds, the fatty acid profile and oxidative stability measured by the Rancimat method as input components. The color scale of scores (cultivars) represents their oxidative stability classification. The violet-red cultivars tend to be much more stable than the blue cultivars.

RANCIMAT – olive oil oxidative stability expressed in hours; Phenolic sum – the sum of all phenolic compounds analyzed; AOleAgly – Aldehydic open forms of oleuropein aglycone; MAOleAgly – Monoaldehydic closed form of oleuropein aglycone; ALigAgly – Aldehydic open forms of ligstroside aglycone; MALigAgly – Monoaldehydic closed form of ligstroside aglycone. Pic – Picual, Mix – Mixani, Lev – Levantinka, Fran – Frantoio, Cor – Coratina, Bos – Bosana, Blan – Blanqueta, Arb – Arbosana.



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