Supplementary Information

Pigment profiles of Spanish extra virgin olive oils by ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry

A. Arrizabalaga-Larrañaga(1), P. Rodríguez(2), M. Medina(2), F. J. Santos(1), E. Moyano(1)\*

(1) Department of Chemical Engineering and Analytical Chemistry, University of Barcelona. Av. Diagonal 645, E-08028 Barcelona, Spain

(2) Laboratori Agroalimentari, Generalitat de Catalunya, Vilassar de Mar s/n, 08348 Cabrils, Spain

**\*** Corresponding author: E. Moyano

**Table of Contents**

[**Supplementary Tables** 1](#_Toc35434218)

[**Table S1.** Concentrations (mg kg-1) of the natural pigments (chlorophylls and carotenoids) found in Spanish EVOO samples. 2](#_Toc35434219)

[**Table S2**  Authenticity parameters of Spanish extra virgin olive oil samples. 4](#_Toc35434220)

[**Supplementary Figures** 5](#_Toc35434221)

[**Fig. S1:** Map of Spain with the 5 different regions where samples were collected colored. (Grey: Andalusia, Red: Madrid/Castilla-La Mancha, Yellow: Catalonia, Green: Basque Country, Blue: Canary Islands. 5](#_Toc35434222)

[**Fig. S2**: Profile of the seven pigments (pheophytin *a*, pheophytin *b*, ß–carotene, lutein, ß–cryptoxanthin, violaxanthin and neoxanthin) determined by UHPLC–APCI–HRMS analysis of the Spanish EVOO studied samples. Samples are labelled from 1 to 40, as shown in Table 3. 6](#_Toc35434223)

[**Fig. S3**: Pigment concentration profile from the studied regions of Spain. 7](#_Toc35434224)

[**Fig. S4**: Partial leas square-discriminant analysis (PLS-DA) scores plots of LV1 *vs*. LV2 when using UHPLC-APCI-HRMS pigment profiles as chemical descriptors. 7](#_Toc35434225)

# **Supplementary Tables**

## **Table S1.** Concentrations (mg kg-1) of the natural pigments (chlorophylls and carotenoids) found in Spanish EVOO samples.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Variety | β-CAR(mean ± SD) | PHE-*a*(mean ± SD) | PHE-*b*(mean ± SD) | LUT(mean ± SD) | β-CRYPT(mean ± SD) | VIO(mean ± SD) | NEO(mean ± SD) |
|  |  | ***From Andalusia*** |
| **1** | Picual | 5.8 ± 0.6 | 8.5 ± 0.5 | 0.68 ± 0.01 | 5.3 ± 0.1 | nd | nd | nd |
| **2** | Picual | 3.8 ± 0.2 | 11 ± 2 | 0.5 ± 0.1 | 3.4 ± 0.6 | 2.3 ± 0.1 | 0.59 ± 0.04 | 0.59 ± 0.04 |
| **3** | Picual | 3.6 ± 0.3 | 8.2 ± 0.5 | 0.42 ± 0.09 | 5.1 ± 0.3 | 2.1 ± 0.2 | 1.2 ± 0.1 | 1.1 ± 0.1 |
| **4** | Picual | 4.0 ± 1.7 | 7.1 ± 0.4 | 0.4 ± 0.1 | 4.2 ± 0.9 | 2.5 ± 0.3 | 1.36 ± 0.01 | 1.34 ± 0.01 |
| **5** | Cornicabra | 2.8 ± 0.4 | 7.4 ± 0.7 | 0.4 ± 0.1 | 3.9 ± 0.2 | 2.7 ± 0.3 | 1.0 ± 0.1 | 0.9 ± 0.1 |
| **6** | Arbequina | 2.5 ± 0.5 | 5.75 ± 0.09 | 0.29 ± 0.06 | 2.6 ± 0.1 | nd | 0.54 ± 0.02 | 0.80 ± 0.03 |
| **7** | Hojiblanca | 2.9 ± 0.6 | 6.7 ± 0.6 | 0.4 ± 0.1 | 3.4 ± 0.2 | nd | 0.7 ± 0.03 | 0.68 ± 0.04 |
| **8** | Hojiblanca | 2.2 ± 0.2 | 7.7 ± 1.2 | 0.5 ± 0.1 | 5.6 ± 0.9 | nd | 0.4 ± 0.02 | 0.43 ± 0.01 |
|  |  | ***From Madrid / Castilla-La Mancha*** |
| **9** | Picual | 3.2 ± 0.6 | 5.2 ± 0.1 | 0.25 ± 0.08 | 2.6 ± 0.3 | nd | 0.8 ± 0.1 | 0.87 ± 0.06 |
| **10** | Picual | 2.5 ± 0.1 | 5.9 ± 0.8 | 0.26 ± 0.01 | 4.7 ± 0.6 | nd | 0.61 ± 0.06 | 0.62 ± 0.06 |
| **11** | Picual | 1.57 ± 0.09 | 5.7 ± 0.4 | 0.34 ± 0.09 | 2.9 ± 0.2 | nd | nd | nd |
| **12** | Arbequina | 2.4 ± 0.2 | 4.9 ± 0.8 | 0.31 ± 0.08 | 2.4 ± 0.5 | nd | 0.37 ± 0.09 | 1.12 ± 0.05 |
| **13** | Arbequina | 2.9 ± 0.5 | 6.4 ± 0.7 | 0.4 ± 0.1 | 4.43 ± 1.4 | nd | 0.5 ± 0.1 | 0.5 ± 0.1 |
| **14** | Arbequina | 3.7 ± 0.6 | 8 ± 1 | 0.7 ± 0.2 | 4.4 ± 0.5 | nd | 0.9 ± 0.1 | 0.8 ± 0.1 |
| **15** | Cornicabra | 1.51 ± 0.03 | 4.6 ± 0.7 | 0.26 ± 0.06 | 2.2 ± 0.2 | nd | 0.12 ± 0.01 | 0.11 ± 0.02 |
| **16** | Picual | 1.9 ± 0.1 | 5.67 ± 0.06 | 0.31 ± 0.08 | 2.8 ± 0.6 | nd | 0.41 ± 0.04 | 0.43 ± 0.04 |
|  |  | ***From Catalonia*** |
| **17** | Arbequina | 3.1 ± 0.4 | 7.9 ± 1.9 | 0.4 ± 0.3 | 3.2 ± 0.3 | nd | nd | nd |
| **18** | Arbequina | 2.2 ± 0.1 | 6.29 ± 1.6 | 0.3 ± 0.1 | 2.3 ± 0.3 | nd | nd | nd |
| **19** | Arbequina | 1.5 ± 0.3 | 8 ± 2 | 0.5 ± 0.1 | 5.3 ± 0.7 | nd | 1.1 ± 0.1 | 1.2 ± 0.1 |
| **20** | Arbequina | 3.5 ± 0.8 | 8.3 ± 0.5 | 0.63 ± 0.03 | 4.4 ± 0.9 | nd | 1.35 ± 0.01 | 1.32 ± 0.01 |
| **21** | Arbequina | 5.4 ± 0.3 | 6.6 ± 0.1 | 0.34 ± 0.08 | 3.0 ± 0.2 | nd | nd | nd |
| **22** | Arbequina | 7.3 ± 0.6 | 8.1 ± 0.3 | 0.50 ± 0.06 | 2.3 ± 0.1 | nd | 0.62 ± 0.04 | 0.54 ± 0.04 |
| **23** | Arbequina | 3.5 ± 0.9 | 6.7 ± 0.9 | 0.38 ± 0.07 | 2.1 ± 0.4 | nd | 0.2 ± 0.3 | 0.1 ± 0.2 |
| **24** | Arbequina | 7 ± 1 | 7.4 ± 0.2 | 0.30 ± 0.05 | 3.1 ± 0.1 | nd | 0.83 ± 0.05 | 0.69 ± 0.06 |
|  |  | ***From Basque Country*** |
| **25** | Arroniz | 1.4 ± 0.2 | 14 ± 2 | 0.74 ± 0.04 | 5.6 ± 0.8 | 3.3 ± 0.2 | 1.37 ± 0.03 | 1.34 ± 0.03 |
| **26** | Arbequina | 1.0 ± 0.1 | 8.2 ± 0.5 | 0.54 ± 0.07 | 3.5 ± 0.1 | 2.5 ± 0.1 | 0.92 ± 0.04 | 0.87 ± 0.06 |
| **27** | Arbequina | 6 ± 1 | 15 ± 2 | 0.82 ± 0.07 | 13 ± 2 | 3.4 ± 0.1 | 2.3 ± 0.1 | 2.20 ± 0.04 |
| **28** | Arbequina | 4.3 ± 0.4 | 15 ± 3 | 0.71 ± 0.06 | 3.8 ± 0.3 | 2.45 ± 0.08 | 0.14 ± 0.02 | 0.12 ± 0.01 |
| **29** | Arroniz | 2.4 ± 0.3 | 13 ± 2 | 0.63 ± 0.05 | 7.3 ± 0.8 | 3.1 ± 0.3 | 1.45 ± 0.02 | 1.44 ± 0.03 |
| **30** | Arbequina | 5.3 ± 0.3 | 19 ± 2 | 0.82 ± 0.04 | 8.2 ± 0.7 | 3.1 ± 0.3 | 1.43 ± 0.03 | 1.40 ± 0.03 |
| **31** | Arbequina | 2.3 ± 0.2 | 14 ± 1 | 0.67 ± 0.04 | 8 ± 1 | 2.4 ± 0.1 | 1.7 ± 0.2 | 1.7 ± 0.3 |
| **32** | Arroniz | 1.56 ± 0.06 | 12.8 ± 0.7 | 0.63 ± 0.02 | 5.1 ± 0.3 | 2.9 ± 0.1 | 1.34 ± 0.03 | 1.33 ± 0.04 |
|  |  | ***From Canary Islands*** |
| **33** | Picual | 2.9 ± 0.7 | 9.1 ± 0.1 | 0.63 ± 0.06 | 4.2 ± 0.4 | nd | 1.4 ± 0.1 | 1.2 ± 0.1 |
| **34** | Arbequina | 8 ± 1 | 29 ± 3 | 0.68 ± 0.03 | 8 ± 1 | nd | 1.57 ± 0.03 | 1.51 ± 0.02 |
| **35** | Arbequina | 11 ± 2 | 17 ± 3 | 0.72 ± 0.04 | 5.2 ± 0.2 | nd | 1.57 ± 0.03 | 1.7 ± 0.2 |
| **36** | Arbequina | 4.08 ± 0.07 | 13 ± 1 | 0.49 ± 0.09 | 4.1 ± 0.9 | nd | 1.58 ± 0.05 | 1.51 ± 0.06 |
| **37** | Arbequina | 5 ± 1 | 17± 2 | 0.5 ± 0.1 | 5.0 ± 0.8 | nd | 1.37 ± 0.02 | 1.33 ± 0.01 |
| **38** | Picual | 10 ± 2 | 20 ± 2 | 0.7 ± 0.1 | 6.8 ± 0.8 | nd | 1.6 ± 0.3 | 1.5 ± 0.2 |
| **39** | Arbequina | 4.5 ± 0.5 | 19 ± 1 | 0.6 ± 0.1 | 6.4 ± 0.9 | 2.4 ± 0.2 | 1.57 ± 0.06 | 1.7 ± 0.2 |
| **40** | Arbequina | 3.2 ± 0.2 | 32 ± 4 | 0.91 ± 0.08 | 14 ± 2 | 2.4 ± 0.1 | 1.39 ± 0.01 | 1.37 ± 0.02 |

nd: not detected (< MLOD)

## **Table S2** Authenticity parameters of Spanish extra virgin olive oil samples.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| EVOO label | P/C | % Lutein | Lutein/β–carotene |  | EVOO label | P/C | % Lutein | Lutein/β–carotene |
| *From Andalusia* |
| 1 | 0.8 | 47.7 | 0.9 |  | 5 | 0.8 | 33.9 | 1.4 |
| 2 | 1.0 | 31.9 | 0.9 |  | 6 | 0.9 | 40.6 | 1.0 |
| 3 | 0.7 | 38.8 | 1.4 |  | 7 | 0.9 | 44.0 | 1.2 |
| 4 | 0.6 | 31.6 | 1.0 |  | 8 | 1.0 | 64.8 | 2.5 |
| *From Madrid / Castilla-La Mancha* |
| 9 | 0.7 | 35.0 | 0.8 |  | 13 | 0.8 | 53.3 | 1.5 |
| 10 | 0.7 | 55.3 | 1.8 |  | 14 | 0.9 | 44.8 | 1.2 |
| 11 | 1.3 | 65.1 | 1.9 |  | 15 | 1.2 | 55.4 | 1.4 |
| 12 | 0.8 | 38.6 | 1.0 |  | 16 | 1.1 | 50.5 | 1.5 |
| *From Catalonia* |
| 17 | 1.3 | 51.2 | 1.1 |  | 21 | 0.8 | 35.9 | 0.6 |
| 18 | 1.3 | 52.7 | 1.1 |  | 22 | 0.8 | 21.1 | 0.3 |
| 19 | 0.9 | 57.8 | 3.4 |  | 23 | 1.2 | 36.2 | 0.6 |
| 20 | 0.8 | 41.7 | 1.3 |  | 24 | 0.7 | 26.6 | 0.5 |
| *From Basque Country* |
| 25 | 1.1 | 42.9 | 3.9 |  | 29 | 0.8 | 46.4 | 3.0 |
| 26 | 1.0 | 39.9 | 3.4 |  | 30 | 1.0 | 42.1 | 1.5 |
| 27 | 0.9 | 48.7 | 2.1 |  | 31 | 1.1 | 48.1 | 3.2 |
| 28 | 1.5 | 35.4 | 0.9 |  | 32 | 1.1 | 41.9 | 3.3 |
| *From Canary Islands* |
| 33 | 1.0 | 42.9 | 1.4 |  | 37 | 1.3 | 40.0 | 1.0 |
| 34 | 1.5 | 40.3 | 0.9 |  | 38 | 1.0 | 33.5 | 0.7 |
| 35 | 0.9 | 27.3 | 0.5 |  | 39 | 1.2 | 38.4 | 1.4 |
| 36 | 1.2 | 36.3 | 1.0 |  | 40 | 1.2 | 62.5 | 4.4 |

# **Supplementary Figures**



## **Fig. S1:** Map of Spain with the 5 different regions where samples were collected colored. (Grey: Andalusia, Red: Madrid/Castilla-La Mancha, Yellow: Catalonia, Green: Basque Country, Blue: Canary Islands.



## **Fig. S2**: Profile of the seven pigments (pheophytin *a*, pheophytin *b*, ß–carotene, lutein, ß–cryptoxanthin, violaxanthin and neoxanthin) determined by UHPLC–APCI–HRMS analysis of the Spanish EVOO studied samples. Samples are labelled from 1 to 40, as shown in Table 3.



## **Fig. S3**: Pigment concentration profile from the studied regions of Spain.



## **Fig. S4**: Partial leas square-discriminant analysis (PLS-DA) scores plots of LV1 *vs*. LV2 when using UHPLC-APCI-HRMS pigment profiles as chemical descriptors.