

SUPPLEMENTARY MATERIALS

Results of near UV-Vis spectroscopy: comparison between different fitting models

The original near-UV spectra of olive oils can be deconvoluted by using different models (Domenici et al 2014, Buti, 2016, Borrello et al., 2019). Models 1 and 2 are more appropriate for not fresh olive oils, while models 3 and 4 are more appropriate for fresh olive oils.

- Model 1 includes four main pigments (β -carotene, lutein, pheophytin a and pheophytin b);
- Model 2 includes five main pigments (β -carotene, lutein, cis-neoxanthin, pheophytin a and pheophytin b).
- Model 3 includes four main pigments (β -carotene, lutein, chlorophyll a and chlorophyll b);
- Model 4 includes five main pigments (β -carotene, lutein, chlorophyll a and chlorophyll b).

Table S1. Average R-square values of EVOO 1 in the four models at different sampling time. Model 1 corresponds to four pigments' model (EVOO after some months of storage); Model 2 corresponds to five pigments' model (EVOO after some months of storage); Model 3 corresponds to four pigments' model (EVOO fresh pressed); Model 4 corresponds to five pigments' model (EVOO fresh pressed).

Days after pressing	48	168	197	230	286
	Average R-square				
Model 1	0.996405	0.997816	0.997555	0.997570	0.997449
Model 2	0.996866	0.998881	0.998539	0.998975	0.998859
Model 3	0.995768	0.997144	0.996685	0.996816	0.996649
Model 4	0.996663	0.998668	0.998244	0.998758	0.998640

Table S2. Average R-square values of EVOO 2 in the four models at different sampling time. Model 1 corresponds to four pigments' model (EVOO after some months of storage); Model 2 corresponds to five pigments' model (EVOO after some months of storage); Model 3 corresponds to four pigments' model (EVOO fresh pressed); Model 4 corresponds to five pigments' model (EVOO fresh pressed).

Days after pressing	48	168	197	230	286
	Average R-square				
Model 1	0.996768	0.997095	0.997096	0.997101	0.997069
Model 2	0.998016	0.998097	0.998172	0.998260	0.998291
Model 3	0.996066	0.996120	0.995987	0.996034	0.995939
Model 4	0.997927	0.997695	0.997731	0.997852	0.997866

Table S3. Average R-square values of EVOO 3 in the four models at different sampling time. Model 1 corresponds to four pigments' model (EVOO after some months of storage); Model 2 corresponds to five pigments' model (EVOO after some months of storage); Model 3 corresponds to four pigments' model (EVOO fresh pressed); Model 4 corresponds to five pigments' model (EVOO fresh pressed).

Days after pressing	48	168	197	230	286
	Average R-square				
Model 1	0.995166	0.997827	0.997460	0.997673	0.996291
Model 2	0.995335	0.998771	0.998536	0.998721	0.996535
Model 3	0.994337	0.997126	0.996596	0.996942	0.995237
Model 4	0.995033	0.998543	0.998262	0.998493	0.996057

Results of ^1H NMR of olive oils in the bulk:

From the analysis of ^1H NMR spectra of olive oils in the bulk (see a selection in Figure S1) the following percentages of fatty acids are obtained for the EVOO samples.

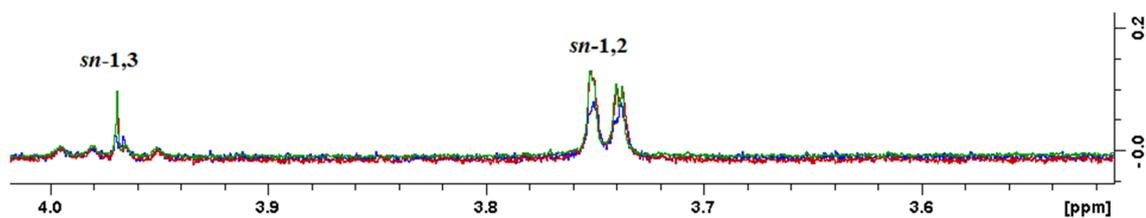


Figure S1. ^1H NMR spectral region showing diglycerides signals (DGs). Blue line corresponds to EVOO 1, red line to EVOO 2 and green line to EVOO 3. 1,2- diglyceride groups (*sn*-1,2) and 1,3-diglyceride groups (*sn*-1,3).

Table S4.1 Fatty acid data are shown as mean \pm standard deviation. *Saturated acids refer mainly to palmitic and stearic acids.

Fatty acids	EVOO 1	EVOO 2	EVOO 3
Linolenic acid (%)	0.52 \pm 0.03	0.51 \pm 0.02	0.49 \pm 0.03
Linoleic acid (%)	7.56 \pm 0.08	7.99 \pm 0.12	7.91 \pm 0.10
Oleic acid (%)	78.11 \pm 0.57	78.80 \pm 1.37	79.59 \pm 1.24
Saturated* acids (%)	13.80 \pm 0.59	12.69 \pm 1.43	12.08 \pm 1.36

Table S5. Chemical shifts (in ppm) assignment of the ¹H NMR signals in CDCl₃ of protons of some phenolic compounds from literature data (modified from Ruiz-Aracama et al., 2017; Karkoula et al., 2012).

Signal	Compound	Chemical shift (ppm)	Multiplicity	Funcional Group
5	Oleomissional	7.360	dd	=CH-OH (C-3)
		9.190-9.205	os	-CHO (C-1)
		11.780	d	=CH-OH (C-3)
6	Oleokoronal	7.386	dd	=CH-OH (C-3)
		9.207-9.222	os	-CHO (C-1)
		11.764	d	=CH-OH (C-3)
7	5S, 4R- oleuropeindial	9.190-9.205	os	-CHO (C-1)
		9.670	d	-CHO (C-3)
8	5S, 4S- oleuropeindial	9.190-9.205	os	-CHO (C-1)
		9.448	d	-CHO (C-3)
9	Oleacein (3,4-DHPEA-EDA)	9.209	d	-CHO (C-1)
		9.22	d	-CHO (C-1)
		9.615-9.645	os	-CHO (C-3)
10	5S, 4R- ligstrodiol	9.207-9.222	os	-CHO (C-1)
		9.680	d	-CHO (C-3)
11	5S, 4S- ligstrodiol	9.207-9.222	os	-CHO (C-1)
		9.452	d	-CHO (C-3)
12	Oleocanthal (p-HPEA-EDA)	9.223	d	-CHO (C-1)
		9.23	d	-CHO (C-1)
		9.615-9.645	os	-CHO (C-3)
13	p-HPEA-EA (ligstroside aglycone)	9.499	d	-CHO (C-1)
		9.52*	d	-CHO (C-1)
14	3,4-DHPEA-EA (oleuropein aglycone)	9.504	d	-CHO (C-1)
		9.50*	d	-CHO (C-1)
15	Elenolic acid	9.615-9.645	os	-CHO (C-1)
<i>Unknown compounds</i>				
16	Unknown	9.310	d	-CHO
17	Unknown	9.355 (9.37)	d	-CHO

Abbreviations: 3,4-DHPEA-EDA: dialdehydic form of decarboxymethyl elenolic acid linked to hydroxytyrosol (3,4-dihydroxyphenylethanol), p-HPEA-EDA: dialdehydic form of decarboxymethyl elenolic acid linked to tyrosol (4-hydroxyphenylethanol), p-HPEA-EA: ligstroside aglycone 4-hydroxyphenylethanol-elenolic acid, 3,4-DHPEA-EA: oleuropein aglycone 3,4-dihydroxyphenylethanol elenolic acid.

*indicate that there is no agreement about the assignment of these signals